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Effluent Monitoring Procedures: Metals Analyses Student Reference Manual

National Training and Operational Tech. Center, Cincinnati, Ohio

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Training course manual designed for wastewater treatment plant technicians who will be responsible for performing selected metals analyses in treatment plant effluents. Contains procedures for selected analyses including: boron, copper, iron, mercury, sodium and zinc. Procedures are in conformance with EPA approved methods as promulgated in the Code of Federal Regulations.

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EFFLUENT MONITORING PROCEDURES: METALS ANALYSES

This course is designed for wastewater treatment plant technicians who will be responsible for performing the selected analyses.

Using methods approved by the U.S. Environmental Protection Agency for NPDES applications and reports, the student will perform selected metals analyses including: boron, copper, iron, mercury, sodium, and zinc.

Classroom instruction is limited to information about performing the selected analyses and reporting the results. Most of the time is given to laboratory experience for the trainee who uses detailed, stepwise procedures to analyze typical samples.

Those attending this course should be able to use laboratory glassware, and be able to do arithmetic calculations for formulas provided.

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Water Program Operations
National Training and Operational Technology Center

DISCLAIMER

Reference to commercial products, trade names, or manufacturers is for purposes of example and illustration. Such references do not constitute endorsement by the Office of Water Program Operations, U. S. Environmental Protection Agency.

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A PROTOTYPE FOR DEVELOPMENT OF ROUTINE OPERATIONAL PROCEDURES

for the

DETERMINATION OF BORON, CURCUMIN METHOD

as applied in

WASTEWATER TREATMENT FACILITIES
and in the
MONITORING OF EFFLUENT WASTEWATERS

Developed by the

National Training and Operational Technology Center
Municipal Operations and Training Division
Office of Water Program Operations
U.S. Environmental Protection Agency

EFFLUENT MONITORING PROCEDURE: Determination of Boron, Curcumin Method

This operational procedure was developed by:

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B.A. - Edgecliff College

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EFFLUENT MONITORING PROCEDURE: Determination of Boron, Curcumin Method

1. Objective:

   To determine the mg/l concentration of boron in an unfiltered sample.

2. Brief Description of Analysis:

   A sample of water containing boron is acidified with hydrochloric acid and evaporated in the presence of curcumin. The reaction forms a red-colored product called rosocyanine. The rosocyanine is taken up in ethyl alcohol and the red color in the solution is compared to that of standards in a spectrophotometer.

   Calcium, magnesium and other cations interfere with the spectrophotometric measurements. These form salts which will not dissolve in ethyl alcohol, thereby contributing turbidity to the solution of rosocyanine. Such cationic interferences are removed by filtering the samples after rosocyanine is formed and dissolved in the ethyl alcohol.

3. Applicability of this Procedure:

   a. Range of Concentration:

      0.10 to 1.0 mg/liter boron (The range may be extended for samples by dilution.)

   b. Pretreatment of Samples:

      The Federal Register Guidelines do not specify any pretreatment (such as digestion) for determining total boron. A 0.45 micron filtration of samples is specified for determining dissolved boron. This procedure does not include directions for the filtration process.

   c. Treatment of Interferences in Samples:

      The Source of Procedure* cites turbidity caused by hardness cations and nitrate nitrogen concentrations in excess of 20 mg/liter as interferences. This procedure includes directions for removing turbidity in samples but does not include determination and removal of nitrate nitrogen. Consult the Source of Procedure* if the presence of excessive nitrate nitrogen is suspected in samples.

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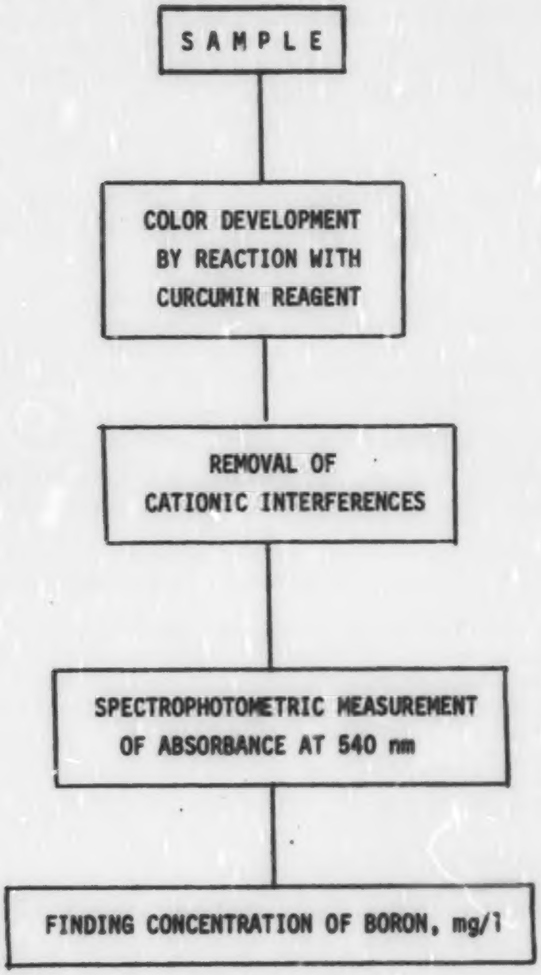
*Source of Procedure: Standard Methods for the Examination of Water and Wastewater, 14th ed., 1976, APHA, Washington, DC, p. 287.

EFFLUENT MONITORING PROCEDURE: Determination of Boron, Curcumin Method

FLOW SHEET


SAMPLE
COLOR DEVELOPMENT BY REACTION WITH CURCUMIN REAGENT
REMOVAL OF CATIONIC INTERFERENCES
SPECTROPHOTOMETRIC MEASUREMENT OF ABSORBANCE AT 540 nm
FINDING CONCENTRATION OF BORON, mg/l

EFFLUENT MONITORING PROCEDURE: Determination of Boron, Curcumin Method

Equipment and Supply Requirements

A. Capital Equipment

1. Balance, analytical with a 0.1 milligram sensitivity.
2. Fume hood or equivalent.
3. Refrigerator capable of maintaining a 4°C temperature.
4. Spectrophotometer for use at 540 nm, with a minimum path length of 1 cm.
5. Water bath, constant temperature to maintain 55 ± 2°C. Size depends on number of samples to be processed along with 5 standards in 100 ml evaporating dishes. Each requires about 5 square inches of space.
6. Water still, metal or a mixed bed ion exchange resin cartridge to prepare boron-free distilled water.

B. Reusable Supplies

NOTE: Glassware made of Corning alkali-resistant glass and storage vessels made of ordinary soft glass have been satisfactory as "boron-free"* glassware.

1. 1 Beaker, 50 ml
2. 1 Bottle, 500 ml, boron-free* glass with stopper.
3. 1 Bottle, 1000 ml, polyethylene with screw cap or boron-free* glass with stopper.
4. 1 Bottle, 5000 ml, polyethylene with screw cap (for distilled water).
5. 1 Cylinder, graduated, 250 ml.
6. Dishes, evaporating, porcelain, 100 ml, 5 plus 1 for each sample to be run.
7. 1 Dropper, 1 to 2 ml with bulb.
8. Flasks, volumetric, 25 ml, with stoppers. 5 plus 1 for each sample.
9. Flasks, volumetric, 100 ml, with stoppers. 6 plus 1 for each sample to be run.
10. 1 Flask, volumetric, 1000 ml, with stopper.
11. Funnels, fluted, 60°, 40 mm diameter, 50 mm stem length. 1 for each sample.
12. 1 Glass rod, short.
13. 1 Mortar and pestle, 70 ml, porcelain (needed only if curcumin is not in finely powdered form).
14. 1 Pipet, measuring, Mohr, 10 ml.
15. Pipets, volumetric, 1.0 ml, 5 plus 1 for each sample.
16. 1 Pipet, volumetric, 2.0 ml.
17. 1 Pipet, volumetric, 4.0 ml.
18. 1 Pipet, volumetric, 5.0 ml.
19. 1 Pipet, volumetric, 8.0 ml. Alternatively, use a 10 ml measuring (Mohr) pipet.
20. 1 Pipet, volumetric, 10.0 ml.
21. 1 Pipet, volumetric, 100.0 ml.
22. 1 Stirring rod (policeman), polyethylene, about 6 inch length.
23. 1 Propipet or pipet bulb.
24. 1 Support, ring stand with small ring (for filtration)
25. 1 Thermometer, degrees C. (To check water bath temperature.)
26. 1 Triangle (for filter funnel).
27. 2 Wash bottles, polyethylene squeeze type.
28. 1 Laboratory apron.
29. 1 Pair safety glasses.

C. Consumable Supplies*

1. 5 Weighing boats (disposable plastic is suitable).
2. Graph paper: 8 1/2 inch by 11 inch with 10 major divisions along the 11 inch side is suitable.
3. Wax pencil.
4. Tissues, lint-free for wiping spectrophotometer cells.
5. Water, distilled, boron-free 2.5 - 3 liters.
6. Boric acid (H_3BO_3), ACS Reagent, anhydrous powder (1 lb unit).
7. Curcumin $[(2\text{-}CH_3OC_6H_3\text{-}1\text{-}OH\text{-}4\text{-}CH{:}CHCO)_2CH_2]$ Eastman No. 1179 or equivalent (25 g unit).
8. 95% Ethyl alcohol (CH_3CH_2OH), Denatured is acceptable (1 gal. or 3 kg unit).
9. Hydrochloric acid (HCl), ACS Reagent, (5 pt. or 7 lb. unit).
10. Oxalic acid ($H_2C_2O_4$), ACS Reagent (1 lb. unit).
11. 1 Box filter paper, Whatman No. 30 or equivalent with diameter to fit filter funnel. (A diameter of 7 cm will fit the filter funnel described in B.)

*NOTE: Use polyethylene or boron-free glass bottles for storage of reagents after preparation.

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
A. Preparing to Test the Sample.	1. Assemble all equipment to be used.	1a. Equipment list is on pp. 6 and 7.	
	2. Check the water bath for maintenance of the 55±2°C temperature required for the test.	2a. Use Procedure B, Checking the Water Bath.	
	3. If necessary, clean all labware to be used for the test.	3a. Use Procedure C, Cleaning Labware.	
		3b. It is usually most convenient to clean labware immediately after performing the test so it is dry and ready for the next use.	
	4. Prepare the reagents for the test.	4a. Use Procedure D, Reagent Preparation.	
	5. Record the identification information for the sample(s).	5a. The sample(s) should be at hand before continuing with the test.	
		5b. Use a laboratory notebook with space for information similar to the "Example Laboratory Data Sheet."	IX Sheet 1 (p. 33)
		5c. In one column for each sample record: "Identification Code, " "Type" (grab or composite), "Date and Time Collected," and the name of the "Sample Collector."	IX.A.5. (p. 33)
	6. Record the date and time you are beginning the analysis.	6a. Use the "Example Laboratory Data Sheet."	IX.A.6. (p. 33)
		6b. In the column(s) of information you recorded for the sample(s).	
	7. Begin the analysis with Procedure E, Preparation of Standards.		

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
B. Checking the Water Bath	1. Fill the water bath to a level where the evaporating dishes for the test can float.	1a. The water bath should be in a fume hood.	
	2. Place a Centigrade thermometer into the water bath.	2a. The thermometer should be reliably accurate.	
	3. Set the temperature regulator to 55°C.		
	4. Turn the bath heating element on.		
	5. Allow the bath to heat to 55°C.	5a. You could start Procedure D, Reagent Preparation, during this time.	
	6. At least ten minutes after the bath reaches 55°C, check the temperature of the water bath.	6a. A longer time is all right. 6b. The temperature should be between 53 and 57°C. 6c. If the temperature is below 53°C, adjust the temperature regulator upward and repeat steps 5 and 6. 6d. If the temperature is above 57°C, adjust the temperature regulator downward and repeat steps 5 and 6.	
	7. Leave the bath turned on.		

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
C. Cleaning Labware	1. All bottles, evaporating dishes, flasks, graduates, pipets, stirring rods, filter funnels and spectrophotometer cells for this procedure should be cleaned using the following steps.	1a. New labware should be cleaned before using it for this test.	
	2. Rinse each item thoroughly with tap water.		
	3. Rinse each item with warm 1:1 hydrochloric acid (HCl) solution.	3a. In a fume hood. 3b. Wear rubber gloves. 3c. CAUTION: Hydrochloric acid and its fumes are hazardous. 3d. The steps to prepare 1:1 hydrochloric acid solution are in D., Reagent Preparation, Reagent 2. 3e. 1:1 nitric acid solution could be used instead.	
	4. Rinse each item thoroughly with tap water.		
	5. Rinse each item with seven individual rinses of boron-free distilled water.	5a. Several rinses with smaller volumes of water are more effective than one or two large-volume rinsings.	
	6. Place items in a clean area to drain dry on clean towels.		

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
D. Reagent Preparation			
1. Boron-free distilled water.	1. Prepare boron-free distilled water.	1a. Use a metal still or a mixed bed ion exchange resin	
		1b. About 5 liters are required for reagents, etc., plus about 1 ml for each standard and sample to be analyzed.	
		1c. Store the water in polyethylene bottles or boron-free glass bottles.	
2. 1:1 Hydrochloric acid solution	1. Measure 250 ml boron-free distilled water.	1a. Use a graduate to measure the water.	
	2. Pour the water into a clean, boron-free 500 ml storage bottle.	2a. Use a polyethylene, screw-capped bottle or a boron-free glass bottle with stopper.	
		2b. The bottle should be cleaned with 1:1 hydrochloric acid solution. To do this, follow these steps using 0.1 of the volumes given, then use Procedure C, Cleaning Labware.	
	3. Measure 250 ml concentrated hydrochloric acid (HCl).	3a. Use a graduate. 3b. In a fume hood. 3c. CAUTION: Hydrochloric acid causes severe burns. Also, the fumes are hazardous and can cause poisoning if inhaled.	
		3d. 1:1 nitric acid could be prepared using these steps if its use for cleaning labware is preferred.	
	4. Slowly pour the acid into the bottle of water, along the inside wall.	4a. To avoid spattering of the mixture.	
	5. Swirl the mixture.	5a. To thoroughly mix the contents.	

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
D. Reagent Preparation (continued)	6. Label the bottle.	6a. This is 1:1 hydrochloric acid. Also, write the date and your name. 6b. This solution is used to clean glassware used in the test procedure.	
3. Curcumin reagent	1. Add about 35 ml of 95% ethyl alcohol (CH_3CH_2OH) to a 100 ml volumetric flask.	1a. You need 4.0 ml of this reagent for each standard and sample to be analyzed.	
	2. Finely grind the curcumin $[(2\text{-}CH_3OC_6H_3\text{-}1\text{-}OH\text{-}4\text{-}CH{:}CHCO)_2CH_2]$ if it is not in this form.		
	3. Weigh out 0.040 g curcumin	3a. Use a weighing boat. 3b. Use an analytical balance.	
	4. Carefully transfer the curcumin to the 100 ml volumetric flask.	4a. Use 95% ethyl alcohol in a squeeze-type wash bottle.	
	5. Swirl the mixture.		
	6. Weigh out 5.0 g oxalic acid ($H_2C_2O_4$).	6a. This oxalic acid intensifies the color of the reaction product and also prevents the formation of interfering colors produced by some metals, if present.	
	7. Carefully transfer the oxalic acid to the same flask.	7a. Again, use 95% ethyl alcohol.	
	8. Swirl the mixture.		

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
D. Reagent Preparation (continued)	9. Measure 4.2 ml concentrated hydrochloric acid (HCl).	9a. Use a graduated pipet.	
	10. Add the acid to the same flask.		
	11. Swirl the mixture.		
	12. Dilute the mixture up to the 100.0 ml mark with 95% ethyl alcohol.		
	13. Stopper the flask.		
	14. Invert the flask several times.	14a. To mix the contents.	
	15. Label the flask.	15a. This is curcumin reagent. Also write the date and your name.	
	16. Store in a refrigerator.	16a. This reagent will be stable up to a week when stored in a cool, dark place.	
4. 95% Ethyl alcohol	1. This needs no preparation but have a supply at hand to perform the procedure.	1a. You need 25 ml for each standard and sample. 1b. Some of the alcohol should be in a squeeze-type wash bottle.	
5. Stock boron solution	1. Add about 500 ml boron-free distilled water to a 1000 ml volumetric flask.		

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
D. Reagent Preparation (continued)			
	2. Weigh out 0.5716 g anhydrous boric acid (H_3BO_3).	2a. Use a weighing boat. 2b. Use an analytical balance. 2c. Do not dry the boric acid in a 103°C oven; it loses weight. Use ACS reagent grade boric acid and keep the chemical bottle tightly stoppered.	
	3. Carefully transfer the boric acid to the 1000 ml flask.		
	4. Swirl the mixture.		
	5. Dilute the mixture up to the 1000.0 ml mark with boron-free distilled water.		
	6. Pour this stock solution into a 1000 ml boron-free reagent bottle.	6a. Use a polyethylene, screw-capped bottle or a boron-free, glass bottle with a stopper.	
	7. Label the bottle.	7a. This is the stock boron solution. 1.00 ml = 100 μg B. Also, write the date and your name on the label.	
	8. Store in a refrigerator.		
6. Standard boron solution	1. Add about 500 ml boron-free distilled water to a 1000 ml volumetric flask.	1a. The standard solution should be prepared fresh each day samples are to be analyzed. 1b. Although small quantities of this solution are required, make one liter to increase the accuracy of its concentration.	

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
D. Reagent Preparation (continued)	2. Measure 100.0 ml of the stock boron solution.	2a. The stock solution must be at room temperature before this measurement is done. 2b. Use a volumetric pipet.	
	3. Deliver the stock solution to the volumetric flask.		
	4. Swirl the flask.		
	5. Dilute the mixture up to the 1000.0 ml mark with boron-free distilled water.		
	6. Label the flask.	6a. This is the standard boron solution. 1.00 ml = 10.0 μg B. Also, write the date and your name on the label.	
E. Preparation of Standards	1. If you are establishing a calibration curve, prepare standards using the following steps. If a calibration curve has already been established, prepare a blank and a check standard beginning below at Step 11.	1a. You should prepare a calibration curve each day you do this test. If several samples are to be analyzed, a blank and a standard to check the curve should be run with each group of samples run after the curve has been prepared.	

<table>
<tr><th>OPERATING PROCEDURES</th><th>STEP SEQUENCE</th><th>INFORMATION/OPERATING GOALS/SPECIFICATIONS</th><th>TRAINING GUIDE NOTES</th></tr>
<tr><td>E. Preparation of Standards (continued)</td><td>2. Mark five 100 ml volumetric flasks with the concentrations of boron, mg/liter which are shown in the second column in Table 2d.</td><td>2a. Flasks must be clean.
2b. Use a wax pencil.
2c. These concentrations are recorded on the "Example Laboratory Data Sheet".
2d. Table 2d.
<table>
<tr><th>Flask</th><th>Boron, mg per liter</th><th>Boron, ml Standard</th></tr>
<tr><td>1</td><td>0.00</td><td>None</td></tr>
<tr><td>2</td><td>0.20</td><td>2</td></tr>
<tr><td>3</td><td>0.50</td><td>5</td></tr>
<tr><td>4</td><td>0.80</td><td>8</td></tr>
<tr><td>5</td><td>1.00</td><td>10</td></tr>
</table></td><td>IX.E.2. (p. 33)</td></tr>
<tr><td></td><td>3. Add about 40 ml boron-free distilled water to each flask.</td><td></td><td></td></tr>
<tr><td></td><td>4. Do not put any standard solution into the flask marked "0.00".</td><td>4a. This flask contains the blank.</td><td></td></tr>
<tr><td></td><td>5. Into each of the remaining marked flasks, pipet the corresponding volume of standard boron solution as shown in the third column in Table 2d.</td><td>5a. The concentration of the standard boron solution is: 1:00 ml = 10.0 μg B.
5b. Use volumetric pipets.</td><td></td></tr>
<tr><td></td><td>6. Do not add any more water to the flask marked "0.00".</td><td>6a. A volumetric measurement is not necessary for the blank at this time.</td><td></td></tr>
</table>

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
E. Preparation of Standards (continued)			
	7. To each of the other 4 flasks, carefully add boron-free distilled water up to the 100.0 ml mark.	7a. Use a squeeze bottle for the final addition of water.	
	8. Put a stopper in each flask.		
	9. Gently invert each flask several times.	9a. To ensure thorough mixing.	
	10. Go to the next Procedure, F. Color Development.		
	11. If a calibration curve has been established, prepare a blank and a check standard using the following steps.	1a. The blank is used to zero the spectrophotometer. 1b. The check standard is compared to the standard curve to check reproducibility.	
	12. Mark one 100 ml volumetric flask "0.00" mg/liter B.	2a. Use a wax pencil.	
	13. Add about 40 ml boron-free distilled water.	3a. This flask contains the blank. 3b. A volumetric measurement is not necessary for the blank at this time.	
	14. Mark a second 100 ml volumetric flask "0.50" mg/liter B.	4a. This concentration is recorded on the "Example Laboratory Data Sheet."	IX.E.14 (p. 33)

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
E. Preparation of Standards (continued)	15. Into this flask, pipet 5.0 ml of the standard boron solution.	15a. The concentration of the standard boron solution is: 1.00 ml = 10.0 μg B. 15b. Use a volumetric pipet.	
	16. Add boron-free distilled water up to the 100.0 ml mark on the flask.	16a. Use a squeeze bottle for the final addition of water.	
	17. Put a stopper in the flask.		
	18. Gently invert the flask several times.	18a. To ensure thorough mixing.	
	19. Go to the next Procedure, F. Color Development.		
F. Color Development of Standards and Sample	1. If you are establishing a calibration curve for the day, use the following steps. If you are using a blank and check standard, begin below at Step 5.		
	2. Mark five 100 ml evaporating dishes with the concentrations of boron, mg/liter which are shown in Table 2e.	2a. Each evaporating dish should be clean, dry, and free from scratches and scoring. 2b. The dishes must be identical in shape, size, and composition to ensure equal evaporation time. 2c. Use wax pencil markings on the outside near the top. 2d. These concentrations are recorded on the "Example Laboratory Data Sheet."	

(continued)

<table>
<tr><th>OPERATING PROCEDURES</th><th>STEP SEQUENCE</th><th>INFORMATION/OPERATING GOALS/SPECIFICATIONS</th><th>TRAINING GUIDE NOTES</th></tr>
<tr><td>F. Color Development of Standards and Sample (continued)</td><td></td><td>2e. Table 2e:
<table>
<tr><th>Dish</th><th>Boron, mg per liter</th></tr>
<tr><td>1</td><td>0.00</td></tr>
<tr><td>2</td><td>0.20</td></tr>
<tr><td>3</td><td>0.50</td></tr>
<tr><td>4</td><td>0.80</td></tr>
<tr><td>5</td><td>1.00</td></tr>
</table></td><td></td></tr>
<tr><td></td><td>3. Pipet 1.0 ml of the 0.00 mg/l B (blank) solution and of each of the standards into the correspondingly marked evaporating dish.</td><td>3a. Use a clean, dry, volumetric pipet for each solution.
3b. The standards were prepared in 100 ml flasks using E, Preparation of Standards.</td><td></td></tr>
<tr><td></td><td>4. Skip Steps 5, 6 and 7 and continue at Step 8.</td><td>4a. These steps are used for a blank and check standard.</td><td></td></tr>
<tr><td></td><td>5. Mark two 100 ml evaporating dishes with the concentrations of boron, mg/liter which are shown in Table 5e.</td><td>5a. Each evaporating dish should be clean, dry, and free from scratches and scoring.
5b. The dishes must be identical in shape, size, and composition to ensure equal evaporation time.
5c. Use wax pencil markings on the outside near the top.
5d. These concentrations are recorded on the "Example Laboratory Data Sheet."
5e.
<table>
<tr><th>Dish</th><th>Boron, mg per liter</th></tr>
<tr><td>1</td><td>0.00</td></tr>
<tr><td>2</td><td>0.50</td></tr>
</table></td><td></td></tr>
</table>

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
F. Color Development of Standards and Sample (continued)	6. Pipet 1.0 ml of the 0.00 mg/l B (blank) into the dish marked "0.00".	6a. Use a clean, dry, volumetric pipet.	
	7. Pipet 1.0 ml of the 0.50 mg per liter standard into the dish marked "0.50".	7a. Use a clean, dry, volumetric pipet.	
	8. Record the sample identification code for the sample.	8a. On the "Example Laboratory Data Sheet" to the left of the blank where "Absorbance" will be recorded for the sample.	IX.F.8. (p. 33)
	9. Mark the sample identification code on a 100 ml evaporating dish.	9a. The dish should be clean, dry, and free from scratches and scoring. 9b. The dish should be identical in shape, size, and composition to the dishes used for the standards. 9c. Make a wax pencil mark on the outside near the top.	
	10. Measure 1.0 ml of the sample (or of diluted sample) into the marked evaporating dish.	10a. For samples containing 0.10 to 1.00 mg per liter boron, use undiluted sample. 10b. For samples containing more than 1.00 mg per liter boron, make an appropriate dilution with boron-free distilled water so that a 1.00 ml portion contains approximately 0.50 μg boron (50 mg per liter). 10c. If the boron concentration of the sample is unknown, you might use 1.00 ml of undiluted sample and also 1.00 ml of a 50% dilution (1:1) of the sample.	

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
F. Color Development of Standards and Sample (continued)			
	11. Repeat Steps 8, 9, and 10 for each sample to be analyzed.	11a. The number of samples that can be analyzed along with the standards depends on the size of the water bath.	
	12. Add 4.0 ml curcumin reagent to each evaporating dish.	12a. Use a volumetric pipet for better control of this alcohol solution. 12b. If you are establishing a standard curve, there are 5 dishes of standards plus the dish(es) of sample(s). 12c. If a standard curve is established, there are 2 dishes of standards plus the dish(es) of sample(s).	
	13. Gently swirl each dish.	13a. To thoroughly mix contents.	
	14. Float the dishes on a water bath set at 55 ± 2ºC and let them remain for 80 minutes to evaporate to dryness.	14a. The water bath should have been checked for maintenance of this temperature and turned on as described in B, Checking the Water Bath. 14b. The temperature is critical to the test. Higher temperatures cause loss of color. 14c. A red-colored product, rosocyanine, is formed. 14d. The odor of hydrochloric acid (HCl) is gone when evaporation is complete. 14e. Keep drying time constant for standards and samples. 14f. The length of drying time critically affects the intensity of color.	
	15. Record the time after 80 minutes have elapsed.	15a. This is the "Time Evaporation Ended" on the "Example Laboratory Data Sheet". 15b. Spectrophotometric readings must be done within the next hour.	IX.F.15. (p. 33)

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
F. Color Development of Standards and Sample (continued)	16. Turn the water bath heating element off.	16a. Unless more samples are to be determined.	
	17. Remove each dish from the water bath.	17a. Be careful that drops of water from the bottom of one dish do not drip into other dishes still in the water bath.	
	18. Carefully wipe the moisture from the bottom of each dish.		
	19. Allow the dishes to cool to room temperature.	19a. Five to 10 minutes.	
	20. Turn on the spectrophotometer.	20a. The instrument can warm up during the next steps.	
	21. Mark 25 ml volumetric flasks with the concentrations of the standards you are running.	21a. If you are establishing a standard curve, mark 5 flasks as 0.00, 0.20, 0.50, 0.80, and 1.00 mg per liter, respectively. 21b. If you are running a blank and check standard, mark 2 flasks as 0.00 and 0.50 mg per liter, respectively.	
	22. Mark 25 ml volumetric flask(s) with the identification code(s) of the sample(s).	22a. If any flasks are not dry, rinse them with 95% ethyl alcohol.	
	23. Add about 7 ml of 95% ethyl alcohol (CH_3CH_2OH) to the dish containing sample.	23a. Use a measuring pipet and very slowly direct the alcohol along the walls of the dish so any spattered solids are washed down to the bottom. 23b. Transfer samples first, then the standards.	

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
F. Color Development of Standards and Sample (continued)			
	24. Use a clean, dry polyethylene rod to gently stir the mixture until all the red-colored product is dissolved.	24a. Keep the mixture in the bottom part of the dish.	
	25. Use a squeeze bottle of 95% ethyl alcohol to rinse the mixture from the tip of the rod into the dish.	25a. Keep in mind that 25 ml is the final volume allowed in the following steps.	
	26. Using a dropper, transfer the solution from the dish into the corresponding 25 ml volumetric flask.	26a. Be careful not to scratch the surface of the evaporating dish with the tip of the glass dropper. 26b. Be careful not to lose any of the solution during the transfer. 26c. A very small funnel can be used for this transfer.	
	27. Add a few ml of 95% ethyl alcohol to the dish.	27a. Use a squeeze-type plastic wash bottle for the alcohol.	
	28. Use the same dropper to transfer this rinse to the corresponding flask.		
	29. Repeat steps 27 and 28 two more times.	29a. Add just a few ml each time to keep within the 25 ml limit of the receiving volumetric flask. 29b. The absence of yellow color from all areas of the dish indicates all original solution has been transferred.	
	30. Remove the bulb from the dropper and rinse 95% ethyl alcohol from the top through the tip and into the flask.		

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
F. Color Development of Standards and Sample (continued)	31. Rinse the outside of the tip of the dropper into the flask.		
	32. Replace the bulb on the dropper.		
	33. Add a few more ml of 95% ethyl alcohol to the dish.		
	34. With the dropper, use this alcohol to bring the volume in the flask to the 25.0 ml mark.		
	35. Put a stopper in the flask.		
	36. Gently invert the flask several times.	36a. To thoroughly mix the contents. 36b. IMPORTANT: Any turbidity in the sample solution(s) at this point interferes with spectrophotometric readings. Use Procedure G to filter sample(s) now.	
	37. Repeat steps 23 through 36 for any other samples, then for the standards in evaporating dishes.	37a. Check that each is transferred to the flask marked with the corresponding sample identification code or concentration.	
	38. Obtain all spectrophotometric readings within one hour of the time evaporation ended by using H, Spectrophotometric Measurements.	38a. The time evaporation ended is recorded on the "Example Laboratory Data Sheet".	

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
G. Removal of Cationic Interferences from the Sample(s)	1. Mark a small receiving vessel with the sample identification code.	1a. Samples should be filtered to remove turbidity. 1b. One of a set of matched spectrophotometer tubes or a very small beaker would be suitable receiver.	
	2. Place a small funnel into a clay triangle on a ring stand support.	2a. A funnel with a 40 mm diameter and a 50 mm stem works well with this volume.	
	3. Flute a piece of filter paper to fit into the funnel.	3a. Use Whatman No. 30 or equivalent filter paper. 3b. A diameter of 7 cm fits the above funnel.	
	4. Place the paper in the funnel.		
	5. DO NOT "wet" the filter paper.	5a. You could change the concentration of the sample.	
	6. Using a small glass rod, transfer the sample from the flask onto the filter paper.	6a. While sample is being filtered, continue with transfers of other samples, then the standards from evaporation dishes to flasks at Step F.23	
	7. DO NOT rinse the original flask and DO NOT add alcohol to the filtered solution.	7a. Adding any alcohol will change the concentration of the sample. You only need about 15 ml of filtered sample to get spectrophotometric readings.	
	8. Remove the receiving vessel from under the funnel.		

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
G. Removal of Cationic Interferences from the Sample(s) (continued)			
	9. Repeat Steps 1 through 8 for each sample being analyzed.	9a. Rinse out the funnel and dry it between uses so no liquid is added to the next sample.	
	10. Obtain spectrophotometric readings within one hour of the time evaporation ended by using H, Spectrophotometric Measurements.	10a. The time evaporation ended is recorded on the "Example Laboratory Data Sheet".	
H. Spectrophotometric Measurements	1. Check that the instrument is warmed up and ready to use.	1a. Allow a warm-up period of approximately 20 minutes (5 minutes minimum). 1b. There is an EMP on "Use of a Spectrophotometer".	
	2. Set the wavelength at 540 nm.		
	3. Set the instrument at infinite absorbance.		
	4. Use the 0.00 mg per liter boron standard to set the instrument at zero absorbance.	4a. Use alcohol for any rinsings of the spectrophotometer tube. 4b. Wipe the outside of the spectrophotometer tube to remove moisture and fingerprints before inserting the tube into the instrument. 4c. Use this same spectrophotometer for standards and samples processed in the same-size evaporating dish as was used to process this blank.	
	5. Remove the 0.00 mg per liter boron standard.		
	6. Check that the scale reading returns to infinite absorbance.	6a. If the reading is not at infinite absorbance, set the control knob until that reading occurs, reinsert the 0.00 mg per liter standard and reset the instrument at zero absorbance. 6b. Then repeat steps 5 and 6.	

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
H. Spectrophotometric Measurements (continued)	7. Record the time.	7a. On the "Example Laboratory Data Sheet" as "Time Absorbances (were) Read".	IX.H.7 (p. 33)
	8. Measure and record the absorbance of each standard.	8a. If you are establishing a standard curve, there are 4 standards. 8b. If a standard curve is established, there is 1 check standard, 0.50 mg per liter. 8c. Keep flasks tightly stoppered when not in use because the alcohol solvent can evaporate, thereby changing the concentration. 8d. Use the same cell for each solution, rinsing it once with alcohol, then two times with the solution to be measured and wiping off the outside before inserting it into the instrument. (You can also use matched cells.) 8e. Record results on the "Example Laboratory Data Sheet" in the column next to Column E.2.	IX.H.8 (p. 33)
	9. Measure and record the absorbance of each sample.	9a. Use the same cell and techniques as in 8d above. 9b. Record the results on the "Example Laboratory Data Sheet" in the column next to Column F.8, the "Sample Identification Code."	IX.H.9 (p. 33)
	10. Turn off the spectrophotometer.		

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
I. Making a Calibration Curve	1. If a calibration curve has been established, omit this Operating Procedure and do Operating Procedure J, Checking the Calibration Curve. If a calibration curve has not been established, do the following steps.	1a. There is an EMP on "Preparation of Calibration Graphs".	
	2. Plot the absorbance values for the four standards obtained in H, Step 8 vs. the concentrations of boron in the calibration standards in E, Step 2.	2a. All this information should be available from the "Example Laboratory Data Sheet". 2b. An example of the axes for the calibration graph is in the Training Guide.	IX. Sheet 1 (p. 33) IX. Sheet 2 (p. 34)
	3. Draw the best straight line through all the points to produce a calibration curve.		
	4. This curve can be used for Procedure K, Finding the Concentration of Boron, mg/liter for the Sample(s).		
J. Checking the Calibration Curve	1. On the calibration curve, locate the absorbance value recorded for the check standard (0.50 mg/liter) in H, Step 8.	1a. This information should be available from the "Example Laboratory Data Sheet" in the column next to "Boron, mg/l in Standards". 1b. The curve was developed in Procedure I, Making a Calibration Curve.	IX. Sheet 1 (p. 33) IX. Sheet 2 (p. 34)
	2. Draw a dotted line over to the calibration curve.		

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
J. Checking the Calibration Curve (continued)	3. From that point on the calibration curve, draw a perpendicular line down to the concentration line.		
	4. Record the concentration of boron, mg/liter at this point for the check standard.	4a. Record the value on the "Example Laboratory Data Sheet" in the column next to the absorbance value for the 0.50 mg/liter standard.	IX.J.4. (p. 33)
	5. Compare this observed concentration of boron, mg/liter to the expected concentration of 0.50 mg/liter.	5a. The observed concentration should be within ±2% of the expected concentration of 0.50 mg/liter. 1) 2% of 0.50 is 0.01. 2) Thus the acceptable range of the observed value is 0.49 - 0.51 mg/liter.	
	6. If the observed concentration of boron, mg/liter is within the acceptable range, the calibration curve can be used for K., Finding the Concentration of Boron, mg/liter for the Sample(s).	6a. If the observed concentration is not 0.49 - 0.51, you can re-run a 0.50 mg/liter check standard and repeat the comparison in Step 5 above. 6b. If the observed concentration still is not 0.49 - 0.51, discard the calibration curve and establish a new one by running standards and constructing a curve. Begin at E.1.	
K. Finding the Concentration of Boron, mg/liter for the Sample(s)	1. On the calibration curve, locate the absorbance value recorded for the sample in H. Step 9.	1a. This information should be available from the "Example Laboratory Data Sheet" in the column next to the "Sample Identification Code."	IX. Sheet 1 (p. 33)
	2. Draw a dotted line over to the calibration curve.	2a. The curve was developed in Procedure I, Making a Calibration Curve.	IX. Sheet 2 (p. 34)
	3. From that point on the calibration curve, draw a perpendicular line down to the concentration line.		

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
K. Finding the Concentration of Boron, mg/liter for the Sample(s) (continued)	4. Record the concentration of boron, mg/liter at this point for the sample.	4a. Record the value on the "Example Laboratory Data Sheet" in the column next to the absorbance value for that sample.	IX.K.4. (p. 33)
	5. Repeat steps 1 through 4 for each sample.		
	6. Sign the "Example Laboratory Data Sheet".	6a. On the line marked "Analyst" in the top section.	IX.K.6. (p. 33)

EFFLUENT MONITORING PROCEDURE: Determination of Boron, Curcumin Method

TRAINING GUIDE

SECTION	TOPIC
I*	Introduction
II	Educational Concepts-Mathematics
III	Educational Concepts-Science
IV	Educational Concepts-Communications
V	Field & Laboratory Equipment
VI	Field & Laboratory Reagents
VII	Field & Laboratory Analysis
VIII	Safety
IX*	Records & Reports

Training guide materials are presented here under the heading marked.
These standardized headings are used throughout this series of procedures.

INTRODUCTION

Section I

	TRAINING GUIDE NOTE	REFERENCES/RESOURCES
	Boron may occur naturally in some waters or may be added to water in certain cleaning compounds or as an industrial waste effluent.	
	The determination of boron in waters, industrial wastes, and sewage effluents is particularly important to agriculture. Boron in small quantities is an essential element for plant growth. However, boron in excess of 2.0 mg/liter in irrigation water is harmful to most plants; some are affected by concentrations as low as 0.75 mg/liter. Drinking waters generally contain less than 0.1 mg/liter. Rarely do they contain more than 1.0 mg/liter which is still considered innocuous for human consumption.	1. Water Quality Criteria, 1972. U.S. EPA Government Printing Office, No. 5501-00520, Washington, DC, p. 341.
	The test described in this instruction can be found in Standard Methods on page 287, entitled 405A. Curcumin Method. This is the only procedure for Boron acceptable for NPDES purposes.	2. Standard Methods for the Examination of Water and Wastewater, 14th ed., 1976, APHA, Washington, DC, p. 287.

RECORDS AND REPORTS

SECTION IX

SHEET 1

EXAMPLE LABORATORY DATA SHEET

Name of Plant ____________________

STEP		SAMPLE	SAMPLE	SAMPLE	SAMPLE
A.5	Identification Code				
A.5	Type (grab or composite)				
A.5	Date and Time Collected				
A.5	Sample Collector				
A.6	Date and Time Analysis Began				
F.15	Time Evaporation Ended				
H.7	Time Absorbances Read				
K.6	Analyst				

E.2 E.14	Concentration of Boron, mg/l in Standards	H.8	Absorbance	J.4	Concentration of Boron, mg/l in Check Standard
	0.00				
	0.20				
	0.50				
	0.80				
	1.00				

F.8	Sample Identification Code	H.9	Absorbance	K.4	Concentration of Boron, mg/l in Sample

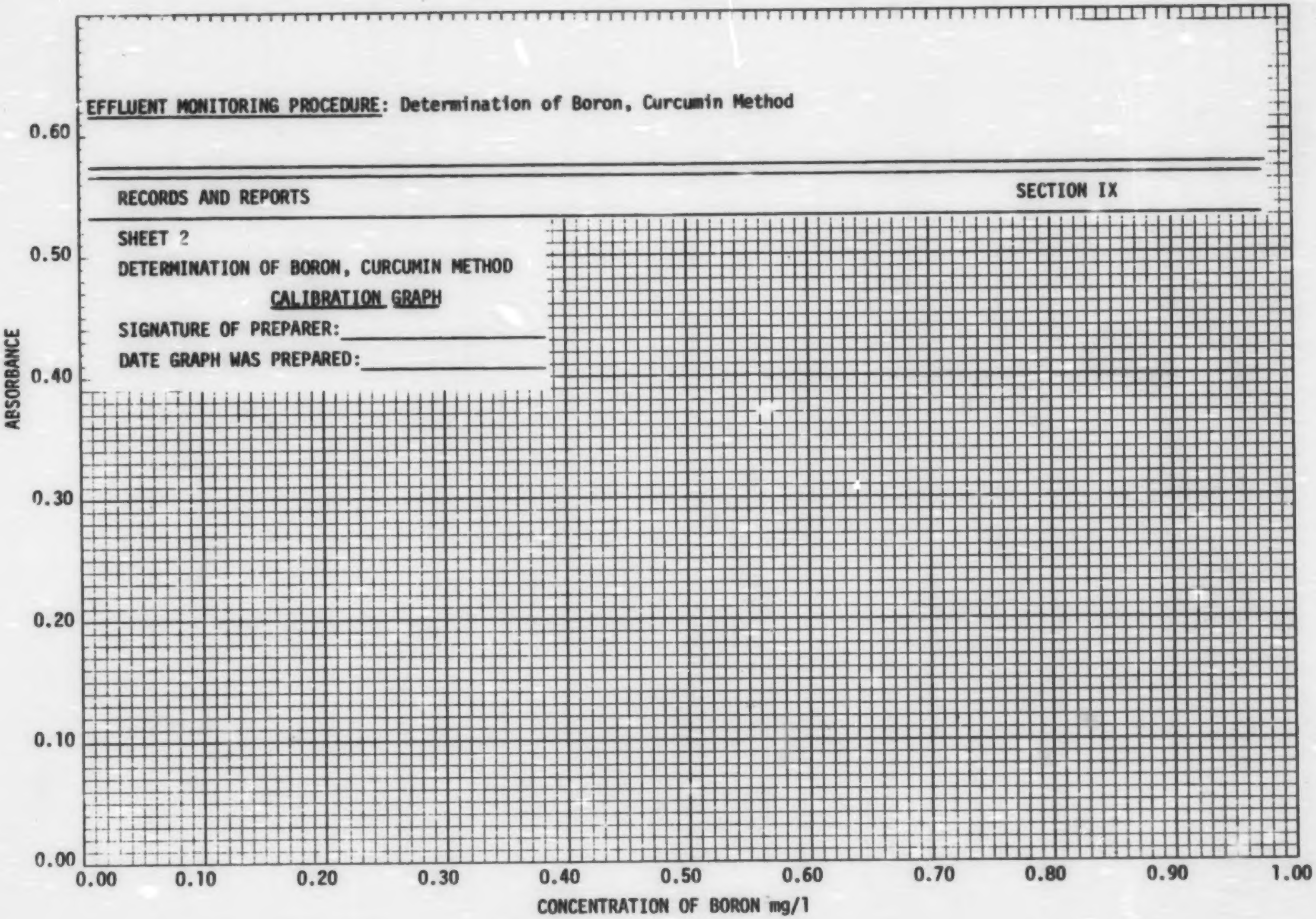
SHEET 2

DETERMINATION OF BORON, CURCUMIN METHOD

CALIBRATION GRAPH

SIGNATURE OF PREPARER:________________

DATE GRAPH WAS PREPARED:________________



A PROTOTYPE FOR DEVELOPMENT OF ROUTINE OPERATIONAL PROCEDURES

for the

DETERMINATION OF TOTAL CALCIUM
(VOLUMETRIC METHOD)

as applied in

WASTEWATER TREATMENT FACILITIES
and in the
MONITORING OF EFFLUENT WASTEWATERS

Developed by the

National Training and Operational Technology Center
Municipal Operations and Training Division
Office of Water Program Operations
U.S. Environmental Protection Agency

EFFLUENT MONITORING PROCEDURE: Volumetric Determination of Total Calcium

This Operational Procedure was developed by:

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MS - Xavier University, Cincinnati, Ohio

4 years Instructor (Chemistry)

2 years Assistant Director Pollution Abatement Technology Department

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EFFLUENT MONITORING PROCEDURE: Volumetric Determination of Total Calcium

1. Objective:

   To determine the total calcium content of a wastewater effluent sample.

2. Description of Analysis:

   The procedure involves a pretreatment of the sample with nitric acid which eliminates interferences from suspended material normally present in wastewater. The sample is subsequently analyzed by the EDTA titrimetric method. The results are reported as Total Calcium in mg/l.

Source of Procedure: Standard Methods for the Examination of Water and Wastewater, 13th Edition, APHA, AWWA, WPCF, 1971. pages 84, 85, and 416.

Methods for Chemical Analysis of Water and Wastes, 1974 Edition, Methods Development and Quality Assurance Research Laboratory, National Environmental Research Center, Cincinnati, Ohio 45268. pages 82-83.

EFFLUENT MONITORING PROCEDURE: Volumetric Determination of Total Calcium

Equipment and Supply Requirements

A. Capital Equipment

1. Balance - analytical 0.1 mg accuracy
2. Balance - triple beam 0.1 g accuracy
3. pH meter
4. Hot plates must heat to above 100°C

B. Reusable Supplies

1. Beakers - 50 ml, 250 ml, and 600 ml
2. Bottles - storage B/S 8 and 32 oz.
3. Buret - 50 ml
4. Cylinders - graduated, 25 ml, 50 ml and 500 ml
5. Flask - Erlenmeyer, 125 ml, and 500 ml
6. Pipets - Mohr, 2 ml, 5 ml, and 10 ml
7. Pipets - Volumetric, 10 ml and 25 ml
8. Ring stand
9. Flask - Volumetric, 100 ml, 500 ml, and 1000 ml
10. Clamp - Buret
11. Funnel - 60°
12. Plastic wash bottle
13. Measuring spoon - 0.2 g

C. Consumable Supplies

1. EDTA (Ethylenedinitrilotetraacetic acid disodium salt) ($Na_2H_2C_{10}H_{12}O_8N_2 \cdot 2H_2O$)
2. Calcium carbonate ($CaCO_3$) anhydrous powder
3. Hydrochloric acid - concentrated (HCl)
4. Ammonium hydroxide - concentrated (NH_4OH)
5. Methyl red indicator
6. Nitric acid - concentrated (HNO_3)
7. Filter paper (#42)
8. Sodium hydroxide ($NaOH$)
9. Sodium chloride ($NaCl$)
10. Eriochrome blue black R indicator (Calcon)

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
DETERMINATION OF TOTAL CALCIUM (VOLUMETRIC METHOD), mg/l			
A. Equipment Preparation			
1. Glassware Wash-up	1. Clean all glassware in a suitable detergent.	1a. Distilled water drains without leaving any droplets.	
2. Balance Inspection	1. Clean all balances - analytical balance and triple beam balance.	1a. Free of dust and dirt.	
3. pH Meter Inspection	1. Use EMP on pH to calibrate the pH meters.	1a. See EPA-430/1-74-015, Outline #5.	
B. Reagent Preparation			
1. Distilled Water	1. Deionized distilled water should be prepared by passing distilled water through a mixed bed of cation and anion exchange resins.	1a. All reagents and calibration standards should be prepared with this water.	
2. Hydrochloric Acid (HCl 1:1)	1. If metal impurities are present, follow the same distillation procedure as for the nitric acid.		
	2. Pour 400 ml of distilled water in a 1 liter volumetric flask.		
	3. Add 500 ml of concentrated hydrochloric acid to the flask and mix.	3a. Transfer the acid in fume hood.	

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
B. Reagent Preparation (Continued)			
	4. Mix thoroughly.		
	5. Dilute to 1 liter.		
	6. Transfer to a 1 liter storage bottle and label as 1:1 hydrochloric acid (HCl).		
3. EDTA Titrant (0.01M) (Ethylenedinitriolo tetraacetic acid disodium salt) $Na_2H_2C_{10}H_{12}O_8N_2 \cdot 2H_2O$)	1. Weigh 3.723 grams of EDTA in a weighing boat.	1a. One milliliter of 0.01 M EDTA titrant is equivalent to 400.8 μg calcium.	
	2. Dissolve the EDTA in approximately 800 ml of distilled water in a 1 liter volumetric flask.		
	3. Dilute to 1 liter.		
	4. Transfer to a storage bottle and label.		
4. Methyl Red Indicator	1. Weigh 20 mg of methyl red indicator in a weighing boat.		
	2. Dissolve in a mixture of 60 ml of ethyl alcohol and 40 ml of distilled water.		
	3. Transfer the indicator solution to a 100 ml storage bottle and label appropriately.		

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
B. Reagent Preparation (Continued)			
5. Ammonium Hydroxide Solution (NH_4OH 3N)	1. Measure 203 ml of reagent grade ammonium hydroxide (NH_4OH) in a graduated cylinder.		
	2. Transfer to 500 ml of distilled water in a 1 liter volumetric flask.		
	3. Mix the solution and dilute to 1 liter.		
	4. Transfer to a storage bottle and label.		
6. Standard Calcium Solution	1. Weigh 1.000 gram anhydrous calcium carbonate ($CaCO_3$) in a weighing boat.		
	2. Transfer to a 500 ml Erlenmeyer flask.		
	3. Add 1:1 HCl to the flask until all the calcium carbonate has dissolved.		
	4. Add 200 ml distilled water to the flask.		
	5. Boil the flask for a few minutes.	5a. This will expel excess carbon dioxide (CO_2).	
	6. Cool the solution and add 4 drops of methyl red indicator.		

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
B. Reagent Preparation (Continued)			
	7. The color must now be adjusted to an intermediate orange color by adding 3N NH_4OH or 1:1 HCl as required.		
	8. Transfer the solution to a 1 liter volumetric flask and dilute to 1 liter with distilled water.		
	9. Transfer to a storage bottle and label.	9a. This solution is equivalent to 1.00 mg $CaCO_3$ per 1.00 ml.	
7. Sodium Hydroxide Solution (NaOH 1N)	1. Weigh out 40 grams of sodium hydroxide.		
	2. Dissolve in 600 ml of distilled water in a 1 liter volumetric flask.		
	3. Dilute to 1 liter.		
	4. Transfer to a storage bottle and label.		
8. Eriochrome Blue Black R Indicator	1. Grind together 200 mg of Eriochrome Blue Black R dye with 100 grams of solid sodium chloride (NaCl).	1a. Use a mortar and pestle. 1b. 0.2 grams will be used for each titration, it is therefore advantageous to have a 0.2 gram transfer spoon available.	
	2. Store in tightly stoppered bottle.		

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
C. Standardization of EDTA Titrant			
	1. Measure 25.0 ml of the standard calcium solution into a 125 ml Erlenmeyer flask.		
	2. Add 2.0 ml NaOH solution to the flask.	2a. This solution should now be in the pH range of 12-13. 2b. A pH meter may be used to check the solution.	
	3. Transfer 0.2 grams of the Eriochrome Blue Black R indicator to the flask.		
	4. Add the EDTA titrant from the buret slowly and with swirling until the color changes from red through purple to bluish purple to a pure blue.		
	5. Record the ml of EDTA on the data sheet.	5a. If the concentration of EDTA was exactly 0.01M, then the titration should require 25 ml and the value of B in the formula: $\text{mg/l Ca} = \frac{A \times B \times 400.8}{\text{ml sample}}$ would be equal to (1). 5b. B is the mg of $CaCO_3$ equivalent to 1.00 ml of EDTA titrant.	

(Continued)

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
C. Standardization of EDTA Titrant (Continued)		5c. Therefore: $B = \frac{\text{ml of EDTA titrant required in your standardization}}{\text{25 ml}}$ If ml of titrant = 25 ml then B = 25/25 = 1 If ml of titrant = 24 then $B = \frac{24}{25} = \underline{0.96}$	
D. Analysis of Calcium in the sample			
1. Pretreatment of Sample	1. Acidify the sample at the time of sample collection by the addition of conc. Nitric acid to a pH of 2.	1a. The nitric acid should be free from Ca or redistilled. 1b. Use a pH meter to measure.	
	2. Transfer 50 ml of well mixed sample to a 150 ml beaker.	2a. Use a graduated cylinder.	
	3. Add 5 ml of 1:1 hydrochloric acid.	3a. Use a graduated pipet. 3b. The hydrochloric acid should be free from calcium or redistilled.	
	4. Place the beaker on a hot plate and heat at 95°C for 15 minutes.	4a. The sample should not boil during this time.	

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
D. Analysis of Calcium in the sample (continued)			
	5. Cool to room temperature.		
	6. Filter the sample.	6a. Use filter paper. 6b. Filter into a 50 ml graduated cylinder 6c. Wash down the walls of the beaker and add to the flask.	
	7. Adjust the sample volume to 50 ml with distilled water.	7a. Dilute to the mark on the volumetric flask. 7b. The sample is now ready for analysis.	
	8. Transfer the sample to a 125 ml Erlenmeyer flask.	8a. For titration.	
2. Titration	1. Using the digested sample, add 2.0 ml of NaOH (sodium hydroxide) solution to the beaker.	1a. This solution should now be in the pH range of 12-13. 1b. A pH meter may be used to check the solution.	
	2. Transfer 0.2 grams of the Eriochrome Blue Black R indicator to the beaker.	2a. Use a 0.2 gram spoon.	
	3. Add the EDTA titrant from the buret slowly, and with thorough mixing, until the color changes from red through purple to bluish purple to a pure blue.		

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
D. Analysis of Calcium in the sample (continued	4. Record the ml of EDTA on the data sheet.	4a. Calculation of Total Calcium (mg/l) mg/l Total Ca = $\frac{A \times B \times 400.8}{\text{ml of sample}}$ A = ml of EDTA used in titration B = mg $CaCO_3$ equivalent to 1.00 ml EDTA (See C.5 for the value) Example: A = 5.2 ml B = 0.96 ml of sample = 50 mg/l Total Calcium (Ca) = $\frac{5.2 \times 0.96 \times 400.8}{50}$ = 40 mg/l	

A PROTOTYPE FOR DEVELOPMENT OF ROUTINE OPERATIONAL PROCEDURES

for the

DETERMINATION OF COPPER (Cu^{++}), MAGNESIUM (Mg^{++}) MANGANESE (Mn^{++}), AND ZINC (Zn^{++})

as applied in

WASTEWATER TREATMENT FACILITIES
and in the
MONITORING OF EFFLUENT WASTEWATERS

Developed by the

National Training and Operational Technology Center
Municipal Operations and Training Division
Office of Water Program Operations
U.S. Environmental Protection Agency

CH.MET.aa.EMP.1b.7.77

EFFLUENT MONITORING PROCEDURE: Determination of Cu^{++}, Mg^{++}, Mn^{++}, and ZN^{++}

This instructional sequence was developed by:

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16 years HEW-FWPCA-EPA-Chemist

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EFFLUENT MONITORING PROCEDURE:* Determination of Cu^{++}, Mg^{++}, Mn^{++}, and Zn^{++}

1. Analysis Objective:

   To determine the copper, magnesium, manganese and zinc concentration of an effluent.

2. Brief Description of Analysis:

   The sample is digested with concentrated nitric acid and evaporated to dryness. The residue is treated with hydrochloric acid, silicates and other insoluble material are removed by filtration and the sample is analyzed for the total metals of interest by atomic absorption spectrophotometry.

Source of Procedure: Methods for Chemical Analysis of Water and Wastes, 1974, Environmental Protection Agency, Methods Development and Quality Assurance Research Laboratory, Cincinnati, Ohio, p. 82

EFFLUENT MONITORING PROCEDURE: Determination of Cu^{++}, Mg^{++}, Mn^{++}, and Zn^{++}

Operating Procedures:

A. Sample Digestion

B. Reagent Preparation

C. Instrument Calibration

D. Instrumental Analysis

E. Calculations

EFFLUENT MONITORING PROCEDURE: Determination of Cu^{++}, Mg^{++}, Mn^{++}, and Zn^{++}

General Description of Equipment and Supplies Used in the Process

A. Capital Equipment

1. Balance, analytical - sensitivity 0.1 milligram
2. Atomic absorption spectrophotometer
3. pH meter
4. Hot plate, 110 V

B. Reusable Supplies

1. Flasks, volumetric 100 ml, 1000 ml pipets
2. Pipets, volumetric, 50 ml, 3 ml, 1 ml
3. Reagent bottles, glass with glass stopper
4. Anion and cation exchange resin cartridges
5. Beakers, 100 ml
6. pH paper
7. Watch glass
8. Funnel, 80 mm diameter
9. Ring stand and 3 inch ring
10. Graduates 50 ml, 10 ml

C. Consumable Supplies

1. Reagents

    Copper metal (analytical reagent grade)
    Magnesium oxide, analytical reagent grade
    Manganese metal
    Zinc metal

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
A. Sample Digestion	1. Transfer 50 ml of sample into a clean 100 ml beaker.	1a. Use a 50 ml pipet.	
	2. Check the pH using pyhydrion paper.	2a. The pH should be 2.0. If the sample was not acidified upon collection, add 1:1 nitric acid dropwise until the pH is adjusted to 2.0.	
	3. Add 3.0 ml of concentrated nitric acid.	3a. Use a 3 ml pipet. Use a rubber bulb on the pipet.	
	4. Place the beaker on a hot plate.	4a. Adjust the hot plate for medium heat.	
	5. Evaporate to dryness cautiously.	5a. Make certain that the sample does not boil.	
	6. Remove the beaker from the hot plate. Allow it to cool to room temperature and add another 3 ml aliquot of concentrated nitric acid.	6a. Use a 3.0 ml pipet.	
	7. Cover the beaker with a watch glass and place it on the hot plate.		
	8. Increase the temperature of the hot plate so that a gentle reflux action occurs.	8a. Continue heating adding additional acid as necessary, until the digestion is complete (generally indicated by a light colored residue).	
	9. Add 5 ml of 1:1 HCl and again warm the beaker to dissolve the residue.		

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
A. Sample Digestion (Cont'd.)	10. Wash down the beaker walls and watch glass with distilled water.	10a. Use a plastic wash bottle.	
	11. Filter the sample through Whatman #42 filter paper into a clean 100 ml volumetric flask.		
	12. Dilute the flask to the mark with distilled water.		
B. Reagent Preparation			
1. Deionized Distilled Water	1. Prepare by passing distilled water through a mixed bed of cation and anion exchange resins.	1a. Use deionized distilled water for the preparation of all reagents, calibration standards and as dilution water.	
2. Nitric Acid Concentrated (HNO_3)	1. Commercially available reagent grade.		
3. Hydrochloric Acid (HCl) 1:1	1. Prepare a 1:1 solution of reagent grade hydrochloric acid by adding 25 ml of commercially available reagent grade hydrochloric acid to 25 ml of deionized water.	1a. Use a 50 ml graduate	
4. Copper Stock Standard Solution	1. Carefully weigh 1.00 grams of electrolyte copper (analytical reagent grade) on an analytical balance.	1a. Use a plastic weighing dish.	

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
B. Reagent Preparation (Cont'd.)	2. Transfer the copper into a clean 100 ml beaker. Add 15 ml distilled water and 5 ml HNO_3 and dissolve.		
	3. Transfer the solution to a 1000 ml volumetric flask and dilute to the mark with deionized distilled water.	3a. Use a plastic wash bottle to rinse the beaker into the volumetric flask. 3b. One ml equals 1 mg copper (1000 mg/l).	
5. Magnesium Stock Standard Solution	1. Weigh 0.829 grams of magnesium oxide on an analytical balance.	1a. Use a plastic weighing dish.	
	2. Transfer the reagent into a 100 ml beaker and add 15 ml distilled water and 10 ml of concentrated HNO_3.		
	3. After dissolution transfer into a clean 1000 ml volumetric flask and dilute to the mark with deionized water.	3a. Use a plastic wash bottle to rinse the beaker into the volumetric flask. 3b. One ml equals 0.50 mg Mg (500 mg/l).	
6. Manganese Stock Standard Solution	1. Weigh 1.000 grams of manganese metal on an analytical balance.	1a. Use a plastic weighing dish.	
	2. Transfer into a 100 ml beaker. Add 15 ml distilled water.		
	3. Add 10 ml HNO_3 and dissolve.	3a. Warm if necessary.	
	4. Transfer the solution into a 1000 ml volumetric flask.		

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
B. Reagent Preparation (Cont'd.)	5. Dilute to the mark with 1 percent (v/v) HCl.	5a. One percent (v/v) HCl can be made by adding 10 ml HCl to 990 ml of deionized water. 5b. One ml equals 1 mg Mn (1000 mg/l)	
7. Zinc Stock Standard Solution	1. Weigh 1.00 gram of zinc metal on an analytical balance.	1a. Use a plastic weighing dish.	
	2. Transfer into a 100 ml beaker. Add 15 ml distilled water and 10 ml of concentrated HNO_3 and dissolve.	2a. Use a 10 ml graduate.	
	3. Transfer the solution into a 1000 ml volumetric flask and dilute to the mark with deionized distilled water.	3a. Use a plastic wash bottle to rinse the beaker during the transfer. 3b. One ml equals 1 mg Zn (1000 mg/l)	
8. Fuel and Oxidant	1. Commercial grade acetylene is generally acceptable.		
	2. Air may be supplied from a compressed air line, a laboratory compressor, or from a cylinder of commercial air.	2a. Caution: Air supply must be free from oil or other contaminants.	
C. Instrument Calibration	1. Turn on air supply.		
	2. Turn on acetylene supply.		
	3. Turn on instrument and ignite flame.	3a. See instruction manual for your particular instrument.	

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
C. Instrument Calibration (Cont'd.)	4. Turn on power to hollow cathode lamp.	4a. Select lamp for proper metal analysis.	
	5. Select wave length for appropriate metal.	5a. Copper (324.7 nm), magnesium (285.2 nm) manganese (279.5 nm) and zinc (213.9 nm)	
	6. Prepare a series of standard solutions for each metal as follows:		
	Copper Transfer 10.0 ml of stock copper solution into a 100 ml volumetric flask and dilute to the mark with deionized distilled water and shake well.		
	Transfer 0.2, 0.4, 0.6, 0.8, and 1.0 ml of the diluted standard solution into each of five 100 ml volumetric flasks respectively. Dilute to the mark with deionized distilled water and shake well. The concentration of these solutions will be 0.2, 0.4, 0.6, 0.8, and 1.0 mg/l respectively.	Use a 1 ml micro pipet graduated in 0.1 ml.	
	Magnesium Transfer 1.0 ml of stock magnesium standard into a 100 ml volumetric flask and dilute to the mark with distilled water.		

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
C. Instrument Calibration (Cont'd.)	Transfer 0.2, 0.4, 0.6, 0.8, and 1.0 ml of the diluted standard solution into each of five 100 ml volumetric flasks respectively. Dilute to the mark with deionized distilled water and shake well. The concentration of these solutions will be 0.02, 0.04, 0.06, 0.08 and 0.10 mg/l respectively. Manganese Transfer 10.0 ml of stock manganese solution into a 100 ml volumetric flask. Dilute to the mark with deionized distilled water and shake well. Transfer 0.2, 0.4, 0.6, 0.8, and 1.0 ml of the diluted standard into each five 100 ml volumetric flasks respectively. Dilute to the mark with deionized distilled water and shake well. The concentration of these solutions will be 0.2, 0.4, 0.6, 0.8, and 1.0 mg/l respectively. Zinc Transfer 10.0 ml of stock zinc solution into a 100 ml		

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
C. Instrument Calibration (Cont'd.)	volumetric flask. Dilute to the mark with deionized distilled water and shake well. Transfer 0.2, 0.4, 0.6, 0.8, and 1.0 ml of the diluted standard into each of five 100 ml volumetric flasks respectively. Dilute the mark with deionized distilled water and shake well. The concentration of these solutions will be 0.2, 0.4, 0.6, 0.8, and 1.0 mg/l respectively.		
	7. Ignite flame and aspirate standard solutions into the flame.		
	8. Prepare a calibration curve by plotting the concentration of the respective metals against the response for each concentration.	8a. Record the response on a recorder or use the readout provided on the instrument.	
D. Instrumental Analysis	1. Aspirate the unknown solution into the instrument immediately following the aspiration of the standards.	1a. Flame characteristics and instrumental settings should be the same for standards and unknowns.	
	2. Record the response.		

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
E. Calculations	1. Determine the concentration of the metal in the sample by substituting the observed instrumental response on the appropriate calibration curve.		

A PROTOTYPE FOR DEVELOPMENT OF ROUTINE OPERATIONAL PROCEDURES

for the

DETERMINATION OF LEAD BY ATOMIC ABSORPTION USING THE EXTRACTION PROCEDURE

as applied in

WASTEWATER TREATMENT FACILITIES
and in the
MONITORING OF EFFLUENT WASTEWATERS

Developed by the

National Training and Operational Technology Center
Municipal Operations and Training Division
Office of Water Program Operations
U.S. Environmental Protection Agency

EFFLUENT MONITORING PROCEDURE: Determination of Lead by Atomic Absorption Using the Extraction Procedure

This operational procedure was developed by:

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EFFLUENT MONITORING PROCEDURE: Determination of Lead by Atomic Absorption Using the Extraction Procedure

1. Analysis Objectives:

   The learner will determine the lead content of a sample by extracting the sample and determining the results on an Atomic Absorption Spectrophotometer.

2. Brief Description of Analysis:

   The sample is concentrated through chelation and extraction with organic solvents. The method produces a solution which can be run under standard conditions for atomic absorption. The solution is then aspirated directly into any atomic absorption instrument of sufficient sensitivity. This procedure contains directions for the use of an Instrumentation Laboratory Inc.*, Model 153 Atomic Absorption Spectrophotometer.

3. Applicability of this Procedure:

   a. Range of Concentration:

      The extraction procedure is recommended for levels of lead below 100 micrograms per liter.

   b. Pretreatment of Samples:

      This EMP includes the digestion procedure specified in the Federal Register Guidelines to determine total lead concentrations.

   c. Treatment of Interferences in Samples:

      Since this EMP procedure involves chelation and extraction of lead from a water sample into organic solvents, the lead is separated from dissolved materials that might interfere in a direct aspiration. The EMP includes procedures or information about glassware preparation, reagent purity and the exceptional sensitivity of this analysis to turbulence and absorption bands in the flame. The choice of using a 217.0 or 283.3 nm wavelength is also discussed. A section about interferences to atomic absorption spectrophotometry (chemical, dissolved solids, ionization and spectral) can be found in the Source of Procedure.*

* Source of Procedure: Methods for Chemical Analysis of Water and Wastes, 1974, Environmental Protection Agency, Methods Development and Quality Assurance Research Laboratory, Cincinnati, Ohio 45268, Page 89 and 112.

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*Mention of particular brand name does not constitute endorsement by the U.S. Environmental Protection Agency.

EFFLUENT MONITORING PROCEDURE: Determination of Lead by Atomic Absorption Using the Extraction Procedure

A. Preparing to Test the Solution

B. Reagent Preparation

C. Sample Preservation and Handling

D. Instrument Set-Up

E. Solubilization of Sample

F. Preparation of Standard Dilutions

G. Extraction Procedure

H. Instrument Operation

I. Calibration

J. Instrument Shut-down

K. Maintenance

SEE FIGURE 1 ON PAGE 31 IN THE TRAINING GUIDE FOR A "FLOW DIAGRAM FOR THE EXTRACTION METHOD".

EFFLUENT MONITORING PROCEDURE: Determination of Lead by Atomic Absorption Using the Extraction Procedure

General Description of Equipment Used in the Process

A. Capital Equipment

1. Instrumentation Laboratories* Model 153 Atomic Absorption or equivalent
2. Hollow cathode lamp - lead
3. Balance, analytical with a 0.1 milligram sensitivity
4. Pressure regulator valves:

    a. Two stage regulator designed to deliver acetylene with an Inlet CGA 510 connector

    b. Two stage regulator designed to deliver air from cylinder with an Inlet CGA 1340 connector

5. Balance, with a 0.1 or 0.01 gram sensitivity
6. Magnetic stirrer - hot plate and magnet retriever
7. Still, borosilicate glass distillation apparatus
8. Steam bath for 100 ml beakers, 6 plus X samples
9. pH meter (optional) to adjust pH for test

B. Reusable Supplies

1. Six plus one/sample. Beaker 100 ml capacity
2. One for each sample plus one more. Beaker 250 ml capacity
3. Three bottles, dropper, brown glass, 100 ml capacity
4. One bottle reagent, brown glass, 1000 ml capacity
5. Two bottles reagent, clear glass, 500 ml capacity
6. One cylinder, graduated, 250 ml capacity
7. Two cylinders, graduated, 500 ml capacity
8. Two flasks, Erlenmeyer, graduated, 500 ml capacity.
9. Two flasks, volumetric, 1000 ml capacity
10. Four flasks, volumetric, 100 ml capacity
11. Six plus one/sample. Flask, volumetric, wide base, 10 ml capacity
12. One for each sample, very small funnel to filter 3-5 ml
13. Six plus one/sample. Funnel separatory, 250 ml capacity
14. One pipet volumetric, 1 ml capacity
15. One pipet volumetric, 2 ml capacity
16. One pipet volumetric, 3 ml capacity
17. Three pipets volumetric, 5 ml capacity
18. Five pipets volumetric, 10 ml
19. One pipet volumetric, 20 ml
20. Three pipets graduated 1/10, 10 ml
21. One pipet graduated 1/10, 1 ml
22. Two pipets, graduated 1/10, 25 ml
23. One pipet, volumetric, 15 ml
24. One for each sample. Watch glasses, 3.5 inch diameter
25. Instrument manufacturer's manual on the atomic absorption instrument
26. Safety glasses
27. One separatory funnel rack
28. One wash bottle, plastic

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* Mention of a particular brand name does not constitute endorsement by the U.S. Environmental Protection Agency.

C. Consumable Supplies

1. Deionizing column - mixed bed type, such as Barnstead-Ultrapure-red cap (D0809) or Fisher #9-034-3
2. Gases:
   Fuel - acetylene (C_2H_2) - for use with the atomic absorption instrument, "purified" grade, cylinder size (DOT-8AL) 380 cuf, CGA size 510
   Oxidant-air - for use with the atomic absorption instrument, "dry" grade, cylinder size (DOT-3AA2015) 2200 cuf, CGA size 1340
3. Labels for reagent bottles - at least 7
4. Laboratory notebooks
5. Pencil, wax marking
6. Reagents
   a. Ammonium hydroxide (NH_4OH) - a test reagent, purchase reagent grade - 1 pt (473 ml) minimum
   b. Bromphenol blue* - ($C_{19}H_{10}Br_4O_5S$) - a test reagent, purchase ACS grade - 5 gram minimum, may not be needed if pH meter is used to adjust pH
   c. Carbon disulfide - (CS_2), used to prepare a reagent, purchase reagent grade - 1 pint (473 ml) minimum
   d. Chloroform ($CHCl_3$) - used to prepare a reagent, purchase reagent grade, 1 gal (3800 ml) minimum
   e. Ethyl alcohol* - (CH_3CH_2OH) - used to prepare a reagent, purchase denatured - 1 pt (473 ml) minimum (May not be needed if pH meter is used to adjust pH)
   f. Hydrochloric acid (HCl) - used as a reagent, purchase ACS grade, 1 pt (473 ml) minimum
   g. Lead nitrate, anhydrous ($Pb(NO_3)_2$) - used to prepare standards, purchase ACS grade 1/4 pound or 100 grams minimum
   h. Nitric acid (HNO_3) - used as a reagent, purchase ACS grade, 1 pt (473 ml) minimum
   i. Pyrrolidine (C_4H_9N) - a test reagent, purchase reagent grade, 1/4 lb or 100 g minimum can be purchased from Aldrich Chemical Co.
   (Cat. No. P7,380-3)
   940 W. St. Paul Ave.
   Milwaukee, WI 53233
7. Filter paper, Whatman #42 to fit very small funnel

* If Bromphenol blue solution is purchased, these reagents need not be purchased.

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
A. Preparing to Test the Solution	1. Clean all glassware to remove all metals.	1a. All glassware including sample bottles should be washed.	V.A.1. (p. 29)
	2. Assemble equipment to be used.	2a. See the equipment lists contained in this EMP.	I.A.2. (p. 27)
	3. Prepare all reagents for the test.	3a. See procedures, Section B.	
	4. Optimize the atomic absorption instrument.	4a. See procedures, Sections D and H and manufacturer's manual.	
	5. Solubilize the sample(s) and extract the sample(s) and standard dilutions.	5a. See procedures, Sections E, F, and G.	
	6. Aspirate all into the AA.	6a. See procedures, Section I.	
	7. Calculate results and record data.	7a. Record sample information in a lab notebook along with date and time of analysis. 7b. After analysis, record the analytical information beside sample information.	
B. Reagent Preparation			
1. Deionized distilled water	1. Prepare by passing distilled water through a mixed bed of cation and anion exchange resins.	1a. Use deionized distilled water for the preparation of all reagents, standards, blanks, and as dilution water. 1b. Use bed such as "Barnstead-Ultrapure" red cap (D0809) or Fisher #9-034-3.	
2. Nitric acid concentrated	1. No preparation necessary.	1a. Use only reagent grade of analyzed purity.	

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
B. Reagent Preparation (continued)			
3. Nitric acid (1:1 dilution) HNO_3	1. Prepare by adding an equal volume of acid to an equal volume of water (i.e., 250 ml acid to 250 ml water).	1a. Caution: acid should always be added to water so as to avoid spattering. 1b. A graduated Erlenmeyer flask can be used for this preparation.	
4. Hydrochloric acid (0.60 N)	1. Add about 50 ml water to a 100 ml volumetric flask.	1a. Use a reagent grade analyzed acid to avoid contamination. 1b. Caution: protective equipment should be used.	
	2. Pipet 5 ml concentrated HCl to the flask.	2a. Use a 5 ml volumetric pipet.	
	3. Cool and dilute to 100 ml with water.	3a. Store in brown dropper bottle (about 100 ml vol.) before use.	
5. Stock lead solution	1. Dissolve 1.599 g of analytical reagent grade lead nitrate ($Pb(NO_3)_2$) in water.	1a. Weighing should be done on an analytical balance. 1b. All reagents should be labeled with reagent name, concentration, date of preparation. 1c. Concentration of stock is 1 mg Pb/ml. 1d. Use a 1000 ml volumetric flask.	
	2. Add 10 ml concentrated nitric acid (HNO_3)	2a. Use a graduate.	
	3. Dilute to 1 liter with deionized distilled water.		
6. Working lead standard solution	1. Add 500 ml water to a volumetric flask.	1a. Use a 1000 ml volumetric flask. 1b. Should be prepared fresh each day an analysis is to be done.	
	2. Add 10 ml concentrated Nitric Acid (HNO_3).	2a. Use a graduate.	

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
B. Reagent Preparation (continued)			
	3. Add 10.0 ml stock lead solution (Reagent 5) to the flask.	3a. Use a volumetric pipet.	
	4. Dilute to the mark with water.	4a. Concentration is 0.01 mg Pb/ml.	
7. Pyrrolidine dithiocarbamic acid (PDCA)	1. Add 500 ml chloroform to a liter flask.	1a. This reagent should be prepared in a well ventilated area (or hood) 1b. Measure 500 ml with graduated cylinder.	
	2. Add 18 ml of analytical grade pyrrolidine.	2a. Pipet with a graduated pipet. 2b. Generates heat -- cool before proceeding. 2c. For supplier, see chemical list. 2d. CAUTION -- reagent is flammable, toxic and corrosive.	
	3. Add 15 ml of carbon disulfide (CS_2) in small portions with swirling.	3a. Carbon disulfide is very odorous. Prepare in hood or well ventilated area. 3b. Use a measuring pipet. 3c. CAUTION - Heat generated - cool before proceeding.	
	4. Dilute to 1 liter with chloroform.	4a. This solution can be stored for several months if stored in a brown bottle in a refrigerator.	
8. Ammonium hydroxide (NH_4OH) concentrated	1. Pour the concentrated NH_4OH into a glass dropper bottle.	1a. Use a hood to prevent inhalation of fumes. Avoid contact with skin. Wear protective equipment. 1b. Only some drops of this are needed for the pH adjustment of acidified samples. 1c. A brown glass dropper bottle conserves the stability of this reagent.	

EFFLUENT MONITORING PROCEDURE: Determination of Lead by Atomic Absorption Using the Extraction Procedure

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
B. Reagent Preparation (continued)			
9. Ammonium hydroxide (NH_4OH) 2N	1. Dilute 3 ml of concentrated NH_4OH to 100 ml with water.	1a. This reagent should be prepared in the hood to prevent inhalation of fumes. Avoid contact with skin. Wear protective equipment. 1b. Only several drops are needed per sample. 1c. Use a brown dropper bottle to store.	
10. Bromphenol blue indicator	1. Dissolve 0.1 g of the solid in 100 ml of 50% ethyl alcohol.	1a. A platform balance can be used for weighing. 1b. In order to prepare this solution 95% ethyl alcohol should be diluted in half (i.e., 50 ml alcohol to 50 ml water). 1c. This solution is stable indefinately so long as it is kept tightly stoppered to prevent evaporation.	
11. Hydrochloric Acid (1:1 dilution) HCl	1. Prepare by adding an equal volume of acid to an equal volume of water (i.e. 250 ml acid to 250 ml water).	1a. CAUTION: Acid should always be added to water so as to avoid spattering. 1b. CAUTION: Heat is generated. 1c. Use safety glasses.	
C. Sample Preservation and Handling	1. Collect a representative sample.	1a. Collect about 1 liter or 1 quart to assure ample amount for analysis.	
	2. Preserve the sample by adjusting to pH 2. Use 3 ml of 1:1 redistilled nitric acid per liter.	2a. Usually this amount is sufficient. However, some highly buffered waters might require more. 2b. Check the pH of the sample with litmus paper to assure that the pH is 2 or below.	

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
D. Instrument Set-Up			
1. Pre warm-up	1. Prepare the instrument for initial operation.	1a. Reference is made to the manufacturer's manual of instruction. 1b. Check power requirements and availability. 1c. Provide adequate ventilation, including vent over instrument burner. 1d. Provide adequate space for instrument and work area. 1e. Provide drain facility.	
2. Lamp installation	1. Install lead hollow cathode lamp.	1a. The trimpot for the position into which the lamp is installed should be adjusted until the lamp draws its optimum lamp current. Set the lead lamp to 5 mA. 1b. Do not exceed the maximum current rating for the lamp as this can seriously affect its life and stability. 1c. Refer to the operation manual for proper installation procedure.	I.D.2. (p. 28)
3. Burner optimization	1. Attach the necessary tanks of gases to the instrument.	1a. For the lead procedure, acetylene and air are required. Use purified grades of gases. 1b. Attach pressure regulator to each cylinder. Care should be taken to match C.G.A. numbers. 1c. Connect cylinders through the regulators to the rear of the instrument at the marked positions. 1d. All cylinders should be securely chained to prevent them from tipping over.	V.D.3.1a. (p. 29)
	2. Follow manufacturer's instructions and optimize the burner.	2a. The analysis of lead is exceptionally sensitive to turbulence and absorption bands in the flame. Therefore, some care should be taken to position the light beam in the most stable, center portion of the flame. To do this, first adjust the burner to maximize the absorption reading with a lead standard. Then aspirate a water blank and make minute adjustments in the burner alignment to minimize the signal.	

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
E. Solubilization of Sample	1. Acidify the sample with 1:1 nitric acid to a pH of 2 at the time of sample collection.	1a. For most samples, 3 ml of 1:1 HNO_3 per liter of sample lowers the pH sufficiently. 1b. Highly buffered samples require more acid. If in doubt, check the pH.	VII.E.1. (p. 30)
	2. Transfer 200 ml of well mixed sample to a 250 ml beaker.	2a. 200 ml is the usual sample volume for concentrations containing less than 100 μg/liter. 2b. Choose a volume appropriate to the expected level of metals.	
	3. Add 3 ml of concentrated nitric acid to the sample.	3a. Use a 10 ml graduated pipet.	
	4. Place the beaker on a hot plate and cautiously evaporate to dryness.	4a. The sample should not boil during this time.	
	5. Cool the beaker and add another 3 ml portion of the concentrated nitric acid.	5a. Use a 10 ml graduated pipet.	
	6. Cover the beaker with a watch glass and return to the hot plate.		
	7. Increase the temperature of the hot plate so that a gentle reflux action occurs.	7a. This will be indicated by droplets forming on the underside of the watch glass.	
	8. Continue heating until a light colored residue forms.	8a. This will indicate that the digestion is complete. 8b. Additional acid may be required to complete this digestion.	
	9. Add sufficient 1:1 hydrochloric acid (HCl) solution and again warm the beaker to dissolve the residue.	9a. Use a 1 ml graduated pipet. 9b. Use the watch glass again to cover the beaker.	

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
E. Solubilization of Sample (continued)			
	10. Wash down the beaker walls and watch glass with distilled water.		
	11. Filter the sample into a 250 ml graduated beaker.	11a. Use a filter paper such as Whatman #42. 11b. To remove silicates and other insoluble material that could clog the atomizer of the atomic absorption instrument.	
	12. Adjust the volume to 200 ml (or the starting volume size).	12a. The sample is now ready for extraction. 12b. The graduations on the beaker can be used to measure the volume. 12c. Results shall be reported as "total".	
	13. The sample is now ready for the Extraction Procedure (G).		
F. Preparation of Standard Dilutions	1. Prepare a blank and series of standard dilutions in 250 ml separatory funnels.	1a. Using the working lead standard (Reagent 6) prepare the blank and standards using volumetric pipets (1,5, 10, 20 ml) for measuring the working lead standard and a graduated cylinder for the water. Prepare as follows, using Columns A and B.	VII.F.1. (p. 30)

A	B	C	D	E
ml's of Std. in 200 ml.	ml's of water	mg Pb/l conc. in 200 ml	mg Pb/l conc. in final 10 ml	Instrument Reading
0.0	200	0.0	0.0	________
1.0	199	0.050	1.0	________
5.0	195	0.250	5.0	________
10.0	190	0.500	10.0	________
15.0	185	0.750	15.0	________
20.0	180	1.000	20.0	________

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
F. Preparation of Standard Dilutions (continued)		1b. Make sure stopcock on separatory funnel is closed before any addition. 1c. Mark the mls of standard used (A) on the funnels. 1d. These standard dilutions should be prepared fresh for each analysis.	
	2. Carry these standards through the extraction procedure, beginning at G.1, pH adjustment.		
G. Extraction Procedure	1. Place a 250 ml separatory funnel into the ring on the stand.	1a. Check the stop-cock on the separatory funnel to assure that it is closed. NOTE: If a pH meter with two electrodes is to be used to adjust the pH in the next steps, do those steps before adding sample to the separatory funnel. If using a single combination electrode, this can be done in the separatory funnel.	
	2. Add 200 ml of sample to the separatory funnel.	2a. If you have a solubilized sample from Procedure E, pour the 200 ml from the beaker into the funnel, and rinse the beaker into the funnel. 2b. In other cases, use a 500 ml graduated cylinder to measure the necessary volume. Add rinse. 2c. Record sample volume used for analysis. 2d. If use of 200 ml of sample gives results too high to be on scale, a dilution can be made. However, the dilution should be made to provide a 200 ml final volume. 2e. If use of a 200 ml sample gives too low results, more than one sample aliquot can be treated and the extracts combined.	

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
G. Extraction Procedure (continued)			
1. pH adjustment	1. Add 2 drops bromphenol blue indicator to the sample(s) and to each standard.	1a. Should a pH meter be used to adjust the pH, omit steps 1 through 4 and begin at step 5. 1b. Apply each step to each sample and standard.	
	2. Mix well.		
	3. Add ammonium hydroxide drop-wise until a very pale blue color persists.	3a. Use concentrated NH_4OH for acidified samples and standards made with 10 or more ml of acidified working lead standard. Use 2 N NH_4OH for more dilute standards. 3b. The reagents should be in glass dropper bottles for this addition. Use a hood.	
	4. Add 0.6 N hydrochloric acid (Reagent 4) drop-wise until the blue color just disappears.	4a. Use a glass dropper bottle for this addition. The bottle should be labeled HCl-.6N. 4b. Pale yellow color may appear.	
	5. Add 2.0 ml 0.6 N hydrochloric acid (Reagent 4). Stopper and shake.	5a. Use a 2.0 ml volumetric pipet. 5b. If a pH meter is used, add acid until the pH is 2.3. Then, the next procedure will bring the pH to the optimum of 2.8.	
2. Chelation and Extraction	1. Add 5.0 ml pyrrolidine dithiocarbamic acid (PDCA) (Reagent 7)	1a. Use a 5.0 ml volumetric pipet for this step. 1b. This reagent should be allowed to come to room temperature before pipetting, since it will be stored in a refrigerator. 1c. The bottle should be restoppered immediately after use and returned to the refrigerator to prolong usefulness.	
	2. Shake vigorously for 2 min.	2a. CAUTION: Use proper technique with the separatory funnel. The reagent contains volatile solvents and pressure is formed.	

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
G. Extraction Procedure (continued)			
	3. Allow the reagent to settle to the bottom of the separatory funnel.	3a. Enough time should be allowed for complete separation of the two phases. 3b. It may take up to 3 minutes.	
	4. Open stopcock and slowly drain off the reagent phase into a 100 ml beaker.	4a. Mark the beaker with the number of ml used to prepare the standard or with the sample identification code.	
	5. Add a second 5.0 ml of PDCA reagent to the separatory funnel.	5a. The same volumetric pipet can be used for all additions of PDCA to all samples and standards provided caution is used to prevent contamination.	
	6. Shake vigorously for two minutes.		
	7. Allow reagent to settle and separate.	7a. This should take about 2-4 minutes.	
	8. Open stopcock and slowly drain off reagent phase.	8a. The reagent should be drained into the same beaker used in step 4. This will combine both the extraction volumes. 8b. Pale pink color may show in extracts.	
3. Recovery of Complex	1. Evaporate to dryness on a steam bath in a hood.	1a. Residue is light color with possible pale green or blue tinges. 1b. Do not "bake" the residue. 1c. Should take about 10-15 minutes.	
	2. Remove and cool 2 minutes.		
4. Digestion of Complex	1. Add 2 ml concentrated nitric acid (HNO_3)	1a. The concentrated HNO_3 must be a good grade as any lead in the acid will be concentrated along with the sample. 1b. Best carried out in a hood. This is a violent reaction; bubbling, dark brown fumes given off.	

(Continued)

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
G. Extraction Procedure (continued)		1c. Use a measuring pipet and add acid down walls, dropwise at first until most residue dissolves. 1d. Hold beaker at a 45 degree angle and slowly add the acid. Rotate the beaker while adding to effect thorough contact of the acid with the residue.	
	2. Place the beaker on a low temperature hot plate and evaporate just up to dryness.	2a. Care should be taken to remove the beaker when only a very small amount of deep brown liquid remains in the beaker. 2b. The evaporation should take about 8 minutes.	
	3. Remove from hot plate and cool for 2 minutes.		
5. Dissolving the Residue	1. Add 2 ml of 1:1 nitric acid (HNO_3) - Reagent 3.	1a. Use a measuring pipet. 1b. Down inside walls at first.	
	2. Return sample to the low temperature hot plate and heat for 1 minute.	2a. Both standards and samples should be at this point together and carried through this step as it could affect the final concentration of acid.	
	3. Cool and quantitatively transfer the solution to a 10 ml volumetric flask -- bring to final volume mark.	3a. A stirring rod and a plastic wash bottle containing deionized distilled water should be used to wash the beaker for transfer. 3b. A wide base 10 ml volumetric flask is suggested or place the volumetric flask in a beaker to prevent tipping it over. A 10 ml stoppered graduated cylinder can be used instead of a volumetric flask. 3c. Mark the flask or cylinder with the number of ml used to prepare the standard. This is also the mg Pb/l concentration in this final 10 ml. For samples, mark the identification code.	
	4. The sample is now ready for aspiration into the atomic absorption instrument.		

EFFLUENT MONITORING PROCEDURE: Determination of Lead by Atomic Absorption Using the Extraction Procedure

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
H. Instrument Operation	1. Rotate the lamp turret until the lead lamp is in the light path.	1a. See instrument manual for location and explanation of each control or switch. 1b. Figures 2 through 5 in the Training Guide show locations of controls.	VII.H.1. (pp. 32-35)
	2. Depress the power switch to the on position.	2a. Properly connected to the power line, this switch controls all power except that of the hollow cathode lamps. 2b. Figure 3 - location of controls.	
	3. Depress the hollow cathode power switch to the on position.	3a. In the on position, connects the hollow cathode lamps to their power supply. 3b. Figure 3.	
	4. Set mode switch at "A".	4a. Selects the single channel direct readout mode of operation. 4b. See Figure 5.	
	5. Set absorption/emission switch for channel "A" at absorbance.	5a. Selects the negative logarithmic absorbance for channel "A". 5b. See Figure 5.	
	6. Adjust channel "A" hollow cathode lamp current.	6a. For the lead lamp, this should be 5.0 mA. 6b. See Figure 5.	
	7. Adjust burner position.	7a. For the lead analysis a Boling Burner should be used. This is the standard burner head supplied with the IL-153 instrument. 7b. The burner height should be adjusted to 8 mm for lead analysis. 7c. See instrument manual for procedures on burner adjustment.	
	8. Set monochromator to proper wavelength.	8a. For the lead analysis the wavelength should be set for 283.3 nm.	

(Continued)

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
H. Instrument Operation (continued)		8b. The 283.3 nm lead line is about half as sensitive as that of the 217.0 nm line. However, the 283.3 line has less background absorbance and is correspondingly less noisy. Consequently, the operator should experiment to decide which line to use. 8c. See Figure 4 for location of controls.	
	9. Set slit width.	9a. The slit setting for the lead procedure should be 80μ or position 4 on the instrument. 9b. See Figure 4.	
	10. Peak the wavelength.	10a. Turn the wavelength selector and watch the channel "A" Incident Intensity Indicator. Adjust the wavelength selector knob past the indicated wavelength in both directions and note where the maximum upward deflection on the indicator occurs. Place the wavelength adjustment knob at the position where the maximum upward deflection is obtained.	
	11. Set I and Io indicators in the green balance zones.	11a. Adjust the channel "A" incident intensity control to a position so that the indicator needle on the channel "A" indicator rests approximately in the center of the green balance zone at the top of the meter. Adjust the transmitted intensity control so that the indicator needle on the indicator is parallel to the needle on the channel "A" incident intensity indicator. 11b. See Figure 5 for location.	
	12. Ignite the flame.	12a. The section in the manufacturer's manual describing burner operation should be read thoroughly. before attempting to ignite the burner.	

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
H. Instrument Operation (continued)	13. Adjust fuel and oxidant pressures.	13a. For the lead procedures it is recommended that the acetylene pressure be set at 4.5 psig and the air pressure be set at 7.0 psig. This will produce a stoichiometric flame that will produce best results. 13b. The analysis of lead is exceptionally sensitive to turbulence and absorption bands in the flame, particularly for the 283.3 nm band. Therefore, some care must be taken to position the light beam in the most stable, center portion of the flame. To do this, first adjust the burner to maximize the absorbance reading with a lead standard. Then, aspirate a water blank and make minute adjustments in the burner alignment to minimize the signal. 13c. See Figure 3 for location of controls.	
	14. Set scale expansion at 2.5.	14a. Graduated in relative absorbance units, this control allows selection of the instrumental sensitivity. 14b. See Figure 5 for location.	
	15. Set calibration control fully clockwise.	15a. This control is in parallel with the channel "A" Digital display, used with the automatic calibration button to set the appropriate absorbance or concentration level on the display. 15b. See Figure 4 for location.	
	16. Set dampening selector switch at M position.	16a. Selects the settling time of both the digital displays or selects the integration sampling period. The "M" position is equivalent to a ten second time constant in the real-time damping of the readout. 16b. See Figure 5 for location.	

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
H. Instrument Operation (continued)	17. Aspirate blank and depress auto-zero.	17a. Activates the channel "A" zeroing servos, electronically setting I equal to I_o when the blank is aspirated. 17b. See Figure 4 for location.	
	18. Set read/hold switch to read.	18a. Activates the digital display. 18b. See Figure 5 for location.	
	19. Set 0000 with auto-zero zero control.	19a. The zero control sets the channel "A" digital display to zero. 19b. See Figure 4 for location.	
I. Calibration	1. Calibrate the instrument by aspirating the 10 mg/l standard.	1a. The IL Model 153 atomic absorption instrument can be calibrated either in absorbance or concentration. The procedure given is for concentration. 1b. It is assumed the steps in sections F and G have been carried out.	
	2. Depress the auto-cal button while the standard is being aspirated.	2a. See Figure 4 for location. 2b. This activates the calibration mechanism to establish the slope of the absorbance concentration.	
	3. Set the digital display to read 1000.	3a. Use the calibration control to set the digital display if it does not read 1000. 3b. See Figure 4 for location of controls.	
	4. Release the auto-cal button.		
	5. Final adjustment to the concentration read-out should be done with the calibration control without depressing the auto-cal button.	5a. Should different sensitivities be required, the scale expansion switch can provide it.	

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
I. Calibration (continued)	6. Aspirate the rest of the standards.	6a. Record the instrument reading for each standard in Column E on the Table in Procedure F.1a. 6b. A standard curve, plotting the meter display vs. the known concentration (column E vs. column C, Table I) can be made to prove if a straight line relationship is being obtained. 6c. So long as 200 ml portions are used, the calibration as described here will give correct values for the samples in mg/l. Since the standard used to calibrate the instrument was set to read its concentration in mg/l, the dilution factors needed because of using 200 ml and concentrating the sample to 10 ml are incorporated into the instrument calibration. Consequently, no change in the sample size can be done unless the value obtained from the instrument read-out is multiplied by a dilution factor.	
	7. Multiply the resultant concentration by the appropriate dilution factor if the sample has been diluted.	7a. Concentration of sample before dilution = Concentration found from instrument X $\frac{\text{total mls. after dilution}}{\text{mls. of sample taken for dilution}}$	
	8. Aspirate the samples.	8a. Leave the parameters as established by the aspiration of the standards.	
	9. Occasionally re-aspirate the 10.0 mg/l standard.	9a. This will indicate whether the instrument calibration has remained constant. 9b. On re-checking the same calibrating standard, depress the auto-cal button to re-establish the slope of the absorption-concentration relationship.	

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
I. Calibration (continued)	10. Record all analytical data in a laboratory notebook.	10a. Report results to the nearest whole microgram per liter.	
J. Instrument Shut-down	1. If a flame is burning aspirate water for about 15 seconds.	1a. This will prevent build-up of solids in the capillary.	
	2. Close the acetylene cylinder valve.	2a. The flame will automatically extinguish itself, leaving about 9 psig in the acetylene supply line.	
	3. Close the air cylinder valve.		
	4. Depress H.C. switch to off.		
	5. Depress power switch to off.	5a. Caution: Exercise care in touching the burner head and vent area. These will be hot enough to cause serious burns.	
K. Maintenance	1. Clean the instrument regularly.	1a. A regular program of care and maintenance will prolong the life-time and maximize its utility. Such items as filters in gas lines, air intakes, burner compartment, burner, and nebulizer should be cleaned.	
	2. Insure the drain cup is filled each day prior to ignition.	2a. See the instrument manufacturer's manual for exact procedures.	

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
K. Maintenance (continued)	3. Change the acetylene tank when its pressure falls to 75 psig.	3a. This will insure a minimum carry over of any acetone.	
	4. Change O rings in burner body when aspirating organic solvents.	4a. The manual will provide instructions.	

TRAINING GUIDE

SECTION	TOPIC
I*	Introduction
II	Educational Concepts - Mathematics
III	Educational Concepts - Science
IV	Educational Concepts - Communications
V*	Field and Laboratory Equipment
VI	Field and Laboratory Reagents
VII*	Field and Laboratory Analysis
VIII	Safety
IX	Records and Reports

*Training guide materials are presented here under the headings marked *.

	TRAINING GUIDE NOTE	REFERENCES/RESOURCES
A.2.	The atomic absorption determination of lead should be considered as part of the overall determination of the heavy metals. The procedure includes a standard procedure for the metal which utilizes direct aspiration into the atomic absorption instrument. This procedure, however, is limited as to the lower limit which can be measured. The detection limit for the standard procedure is given as 0.5 mg Pb/l; however, the maximum level permitted in potable water is 0.05 mg/l. Consequently, an additional procedure must be carried out--that is, some type of concentration step. When the concentration of the metal is not sufficiently high to determine directly or when considerable dissolved solids are present in the sample, certain of the metals may be chelated and extracted with organic solvents. There is a general procedure available which utilizes a chelating and extraction procedure at distinct pH values to remove all heavy metals from one sample. The procedure here is a modification of this procedure and is specific for the determination of lead. The easiest concentration procedure would involve an evaporation at a low pH of a large volume of sample and then direct aspiration. This procedure is recommended for waters where little interference is present and having a low concentration of solids. The extraction procedure contained in this EMP should be used if the two previous conditions cannot be met in a sample. By using the extraction technique both solids and interfering ions are removed. To just filter such a sample would remove the suspended portion and not give total results. Atomic absorption spectroscopy is similar to flame emission photometry in that a sample is atomized and aspirated into a flame. In atomic absorption a light beam is directed through the flame into a monochromator and onto a detector that measures the amount of light absorbed by the sample. Absorption is more sensitive in most cases because it depends upon the presence of free unexcited atoms which usually have a higher ratio of existence than excited atoms. Since the wavelength of the light beam is characteristic of only the metal being	

determined the light energy absorbed by the sample in the flame is a measure of the concentration of that metal in the sample. This principle is the basis of atomic absorption spectroscopy.

D.2. The spectral source of monochromatic light for atomic absorption analyses is provided by a hollow cathode lamp. As each lamp emits the line spectra of the element it is designed for, a different lamp is used for each element with few exceptions. The lamps are enclosed in a glass envelope filled with an inert gas. The lead lamp uses neon gas at a low pressure (1 to 10 mm Hg). Once sufficient voltage is applied across the electrodes within the lamp, the inert gas ionizes and current begins to flow. When this happens, positive gas ions bombard the cathode and heating occurs. As the inner surface of the cathode heats, it sputters and the metal from which it is made vaporizes and fills the cathode volume. Charged gas particles collide with the metal atoms raising their valance electrons to higher energy states. When these excited electrons return to their ground state, they emit light. The spectrum thus emitted contains the same wavelength of light required for absorption of that metal (lead) atom in the flame.

	TRAINING GUIDE NOTE	REFERENCES/RESOURCES.
A.1.	The procedure for washing glassware should include the following steps: a) Wash with detergent b) Rinse with tap water c) Wash with 1:1 nitric acid (HNO_3) Prepare by adding equal volume of concentrated nitric acid to water--that is, add 500 ml of acid to 500 ml of distilled water. d) Rinse with tap water e) Wash with 1:1 hydrochloric acid (HCl) Prepare by adding an equal volume of concentrated hydrochloric acid (HCl) to water--that is, add 500 ml of acid to 500 ml of distilled water. f) Rinse with tap water g) Rinse with deionized distilled water	Methods for Chemical Analysis of Water and Wastes, 1974. EPA, EMSL. Page 81.
	Chromic acid may be useful to remove organic deposits from glassware; however, the analyst should be cautioned that the glassware must be thoroughly rinsed with water to remove the last traces of chromium and any other metals. Chromic acid should not be used with plastic bottles.	EPA Methods Manual, page 81.
D.3.1a.	As acetylene (CHCH) is packed dissolved in acetone (CH_3COCH_3), cylinders should be stored only in an upright position. The acetone content of the gas typically depends on the cylinder temperature and pressure. Avoid introducing acetone into the instrument. Should this occur the normal flame obtained will have a slight pink tinge and yield an abnormally high background signal. To reduce acetone carry-over, it is desirable to allow acetylene cylinders to stand undisturbed for at least twenty-four (24) hours before use.	Instrumentation Laboratory, Inc., page 3. Instrumentation Handbook 113 Hartwell Ave. Lexington, MA 02173

	TRAINING GUIDE NOTE	REFERENCES/RESOURCES
E.1	The "E" section must be carried out to produce a result for the determination of the total metal. If Section "E" is not carried out, the sample should be filtered through a 0.045 micron filter, extracted and the value reported as dissolved metal.	
F.1	In an effort to reduce the number of separatory funnels necessary for this determination, it is possible to prepare the blank and standards in 200 ml volumetric flasks. Then allow them to remain in the flasks while the sample or samples are carried through steps solubilization and extraction. The standards could then be extracted. Then all, standards, blank, and samples, could be carried through the remaining steps, and brought together at step G.5.2.	

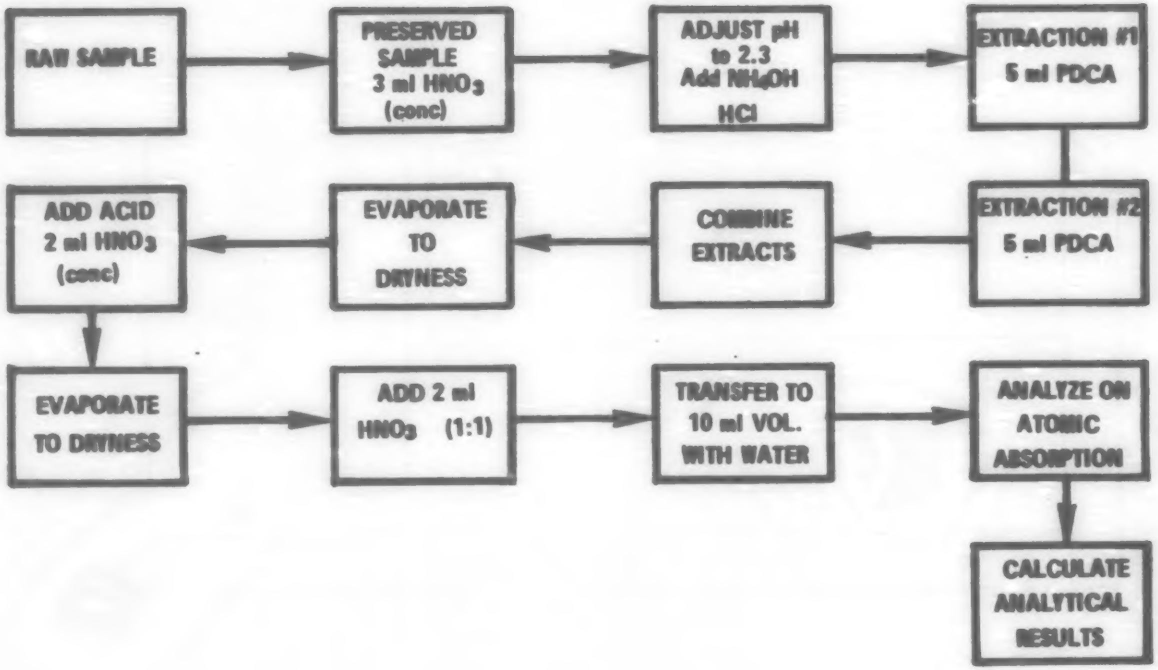
RAW SAMPLE
PRESERVED SAMPLE 3 ml HNO3 (conc)
ADJUST pH to 2.3 Add NH4OH HCl
EXTRACTION #1 5 ml PDCA
EXTRACTION #2 5 ml PDCA
COMBINE EXTRACTS
EVAPORATE TO DRYNESS
ADD ACID 2 ml HNO3 (conc)
EVAPORATE TO DRYNESS
ADD 2 ml HNO3 (1:1)
TRANSFER TO 10 ml VOL. WITH WATER
ANALYZE ON ATOMIC ABSORPTION
CALCULATE ANALYTICAL RESULTS

Figure 1. FLOW DIAGRAM FOR THE EXTRACTION METHOD

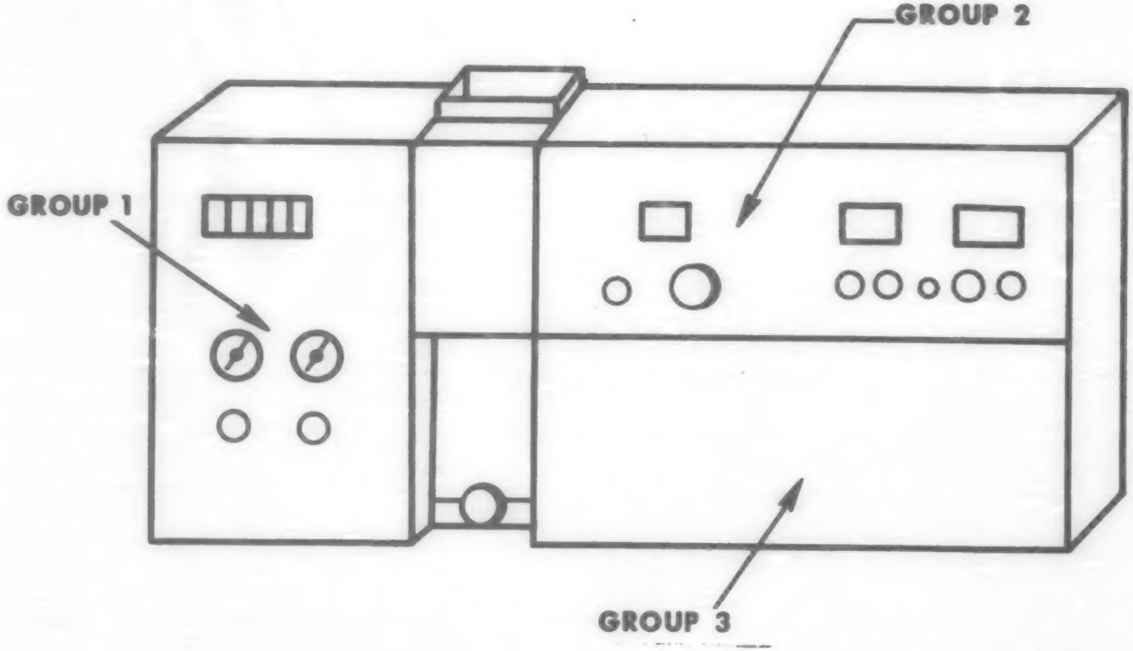
GROUP 1
GROUP 2
GROUP 3

Figure 2. OPERATING CONTROL GROUPS

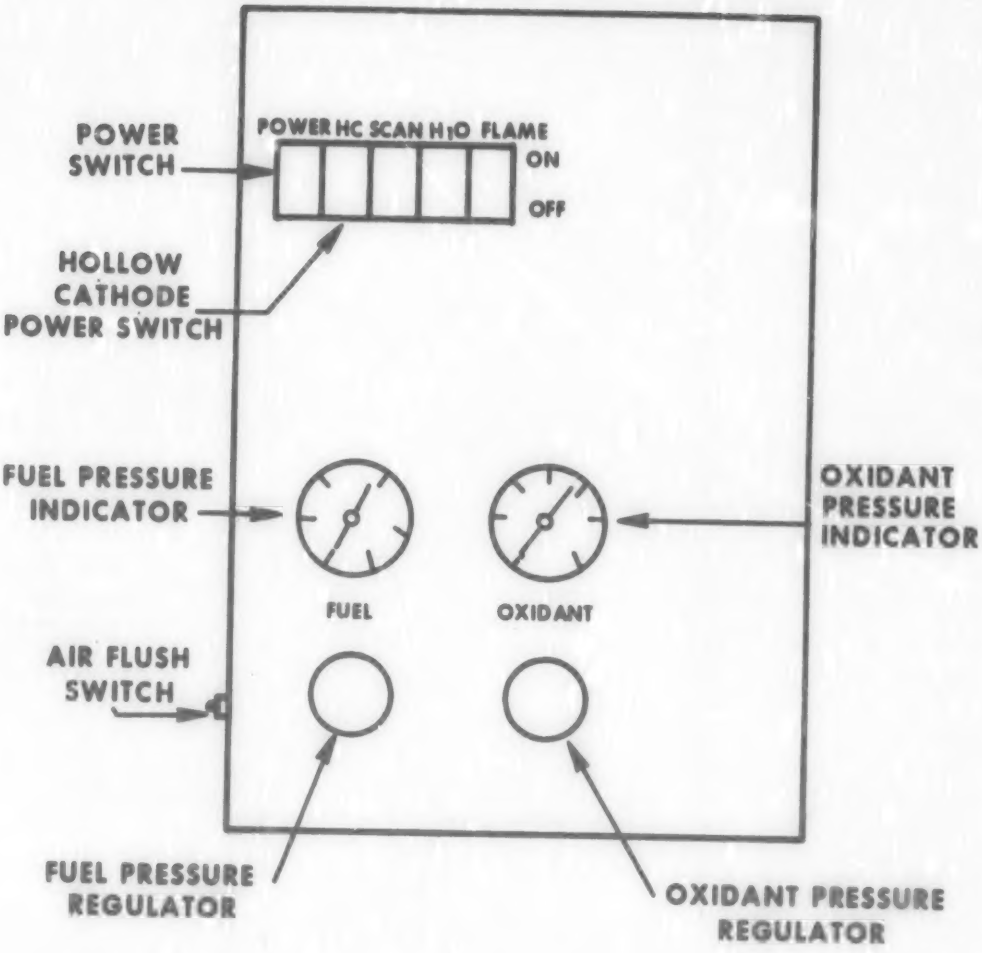
POWER SWITCH
POWER
HC
SCAN
H1O
FLAME
ON
OFF
HOLLOW CATHODE POWER SWITCH
FUEL PRESSURE INDICATOR
OXIDANT PRESSURE INDICATOR
FUEL
OXIDANT
AIR FLUSH SWITCH
FUEL PRESSURE REGULATOR
OXIDANT PRESSURE REGULATOR

Figure 3. LOCATION OF GROUP 1 CONTROLS

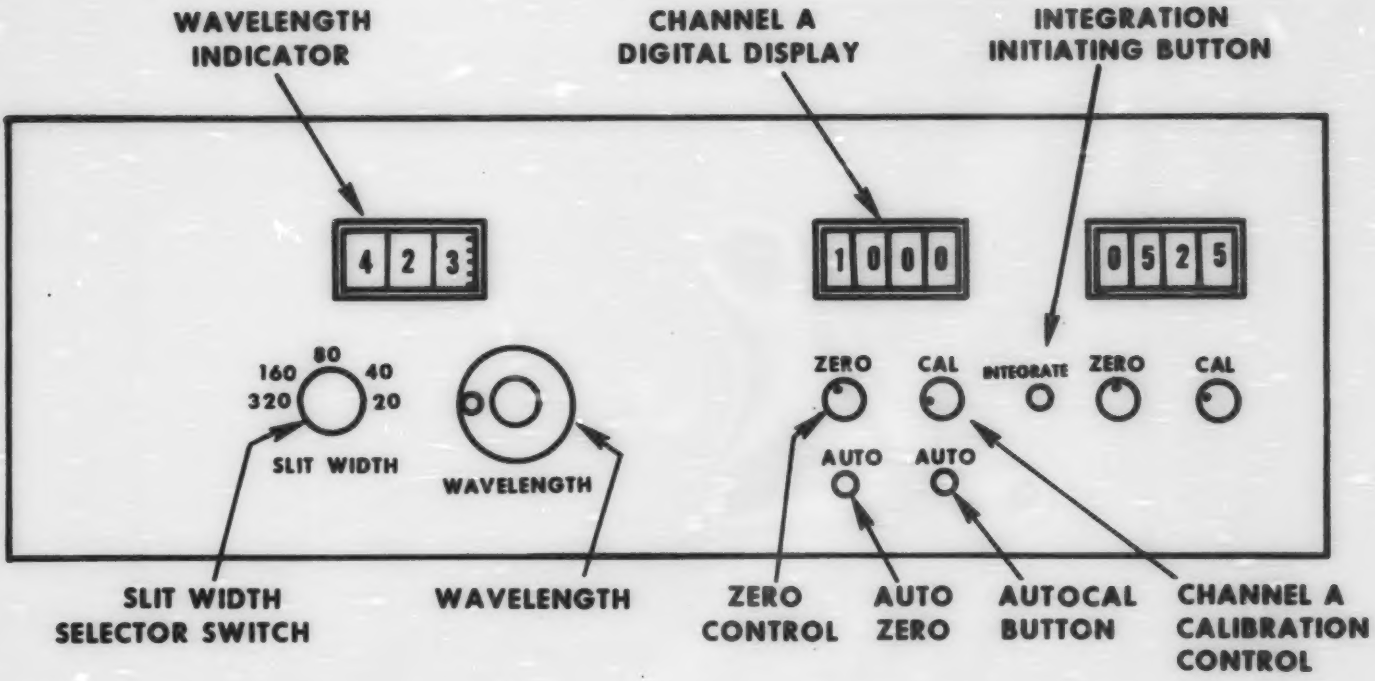
WAVELENGTH INDICATOR
CHANNEL A DIGITAL DISPLAY
INTEGRATION INITIATING BUTTON
4 2 3
1 0 0 0
0 5 2 5
160
80
40
320
20
SLIT WIDTH
WAVELENGTH
ZERO
CAL
INTEGRATE
ZERO
CAL
AUTO
AUTO
SLIT WIDTH SELECTOR SWITCH
WAVELENGTH
ZERO CONTROL
AUTO ZERO
AUTOCAL BUTTON
CHANNEL A CALIBRATION CONTROL

Figure 4. LOCATION OF GROUP 2 CONTROLS

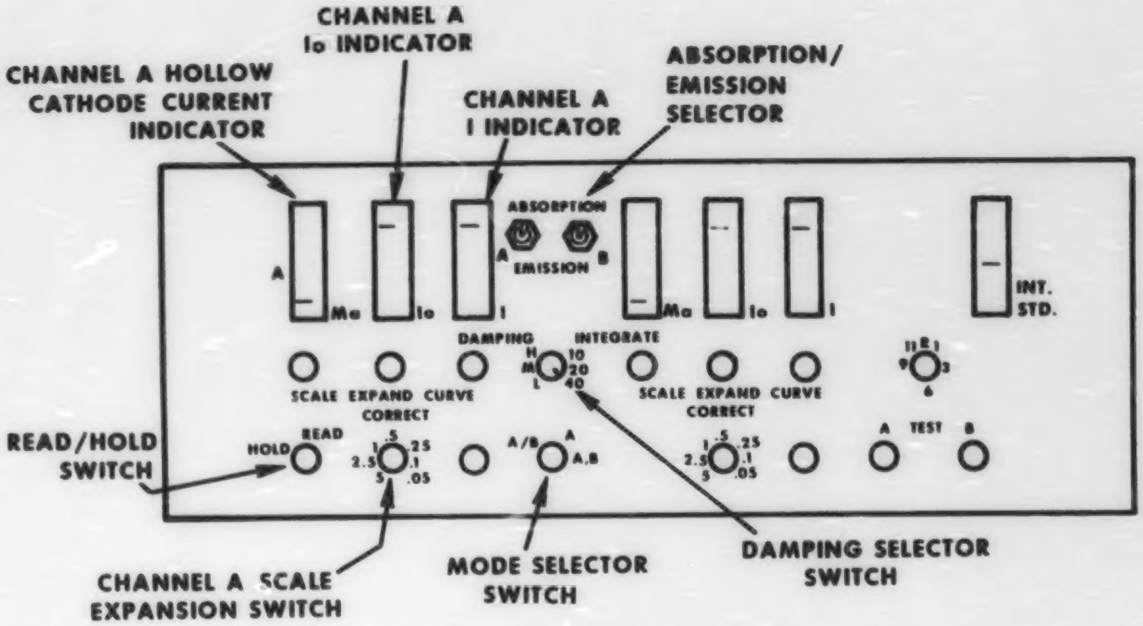
CHANNEL A HOLLOW CATHODE CURRENT INDICATOR
CHANNEL A Io INDICATOR
CHANNEL A I INDICATOR
ABSORPTION/ EMISSION SELECTOR
A
Ma
Io
I
ABSORPTION
EMISSION
A
B
Ma
Io
I
INT. STD.
DAMPING
INTEGRATE
H
M
L
10
20
40
SCALE EXPAND CURVE CORRECT
SCALE EXPAND CURVE CORRECT
11 12 1
9 3
6
READ
HOLD
1 .5 .25
2.5 .1
5 .05
A/B A A.B
1 .5 .25
2.5 .1
5 .05
A TEST B
READ/HOLD SWITCH
CHANNEL A SCALE EXPANSION SWITCH
MODE SELECTOR SWITCH
DAMPING SELECTOR SWITCH

Figure 5. LOCATION OF GROUP 3 CONTROLS

A PROTOTYPE FOR DEVELOPMENT OF ROUTINE OPERATIONAL PROCEDURES

for the

DETERMINATION OF MERCURY USING THE FLAMELESS ATOMIC ABSORPTION (COLD VAPOR) TECHNIQUE

as applied in

WASTEWATER TREATMENT FACILITIES
and in the
MONITORING OF EFFLUENT WASTEWATERS

Developed by the

National Training and Operational Technology Center
Municipal Operations and Training Division
Office of Water Program Operations
U.S. Environmental Protection Agency

EFFLUENT MONITORING PROCEDURE: Determination of Mercury Using the Flameless Atomic Absorption (Cold Vapor) Technique

This operational procedure was developed by:

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POSITION Chemist-Instructor

EDUCATION AND TECHNICAL BACKGROUND

B.S. Chemistry
3 years - Research Chemist
15 years - Training Instructor

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EFFLUENT MONITORING PROCEDURE: Determination of Mercury Using the Flameless Atomic Absorption (Cold Vapor) Technique

1. Analysis Objectives:

The learner will use the attached EMP to place the Coleman Model MAS-50 Mercury Analyzer System into operation including calibration, reagent and sample preparation, and use of the instrument to determine the concentration of mercury in a sample.

2. Brief Description of Analysis:

This procedure is a three step procedure which 1) chemically vaporizes the sample, 2) introduces the mercury and 3) determines the mercury by flameless atomic absorption techniques.

EFFLUENT MONITORING PROCEDURE: Determination of Mercury Using the Flameless Atomic Absorption (Cold Vapor) Technique

Operating Procedures:

A. Equipment Preparation

B. Instrument Set-up

C. Reagent Preparation

D. Sample Handling and Preservation

E. Solubilization of Sample

F. Calibration

G. Sample Determination

H. Calculation

General Description of Equipment Used in the Process

A. Capital Equipment

1. Flameless Mercury Analyzer System - Coleman MAS-50*
   The Coleman MAS-50 is a self contained unit designed to analyze mercury in water and other environments. It is line operated and complete manufacturer's specifications are as follows:

   Sensitivity: 0.01 μg
   Saturation: 9 μg
   Weight: 17 lbs.
   Reproducibility: less than 3%
   Power Requirements: 110/220 volts

2. Analytical balance, 200 gram capacity
3. Trip balance, 500 gram capacity
4. Water bath, capable of maintaining 95°C temperature
5. Recorder (optional) - any multi-range, variable speed recorder that is compatible with the system
6. pH meter and electrodes

B. Reusable Supplies

1. Twelve BOD bottles (one bottle is needed per sample)
2. Volumetric flasks
   - Two 1000 ml
   - Four 100 ml
   - One 250 ml
3. Pipets
   - Three 10 ml volumetric
   - Three 10 ml graduated
   - Three 5 ml graduated
   - Two 1 ml graduated
4. One 100 ml graduated cylinder; one 25 ml graduated cylinder
5. One laboratory apron or coat
6. One pair safety glasses
7. One spatula
8. One pipet bulb
9. One wash bottle for distilled water
10. One glass stirring rod (about 6 inches long)
11. One powder funnel
12. Rubber stoppers - two size #2 (for drying tube)
13. Fifteen ft. Tygon tubing
14. One glass tubing - 6 inches x 3/4 inch diameter
15. One Rotometer (any unit capable of measuring air flow of 1 liter/min.)
16. One set cork hole borers
17. One brush (for cleaning balance)
18. One watch glass for each sample and standard
19. One 150 ml beaker for each sample

*Mention of a specific brand name does not constitute endorsement by the U.S. Environmental Protection Agency.

EFFLUENT MONITORING PROCEDURE: Determination of Mercury Using the Flameless Atomic Absorption (Cold Vapor) Technique

The following equipment is needed depending on which method is chosen to trap the mercury.

a. Liquid Trap

1. Straight glass frit, coarse porosity, such as Corning #404260
2. Filtering flask, such as Corning #40058
3. Rubber stopper, one hole to accept frit
4. Reagents, $KMnO_4$ and H_2SO_4

b. Solid Trap

1. Activated carbon such as Barnebey and Cheney #580-13 or #580-22
   from: Barnebey and Cheney
   E. 8th Avenue & Cassidy St.
   Columbus, OH 43219

   or

   Coleman Instruments
   42 Madison St.
   Maywood, IL 60153
   Item #50-160
2. Glassware: can be assembled similar to the drying tube (B-3) or it can be purchased as catalog no. 50-807 from Coleman Instrument Co. (will include adsorbent)

c. Closed System

The following equipment is needed when using the closed system with a trap.

1. Two position valve, or stopcock, such as Corning #442838
2. Glass "Y" shaped tubing connecter
3. Pinch clamp, type used for stopping flow in tubing

C. Consumable

1. Sulfuric acid (H_2SO_4) concentrated
2. Nitric acid (HNO_3) concentrated
3. Potassium Permanganate, $KMnO_4$
4. Potassium Persulfate, $K_2S_2O_8$
5. Sodium Chloride, NaCl

C. Consumable (Cont'd.)

6. Hydroxylamine Sulfate $(HONH_2)_2 \cdot H_2SO_4$ or
   Hydroxylamine Hydrochloride $NH_2OH \cdot HCl$
7. Stannous Sulfate, $SnSO_4$ or Stannous Chloride, $SnCl_2$
8. Mercuric Chloride, $HgCl_2$
9. Potassium dichromate, $K_2Cr_2O_7$ (for cleaning glassware)
10. Magnesium Perchlorate, $Mg(ClO_4)_2$ for drying tube, 20 g.
11. Distilled water
12. Sponges (for cleaning laboratory table tops)
13. Notebook for recording weights and readings
14. Graph paper, arithmetic (for plotting standard curve)
15. Two pieces of glass tubing (5mm diameter, about two inches long) for the drying tube
16. Glass wool (for drying tube)
17. Plastic weighing boats
18. Pen or pencil

EFFLUENT MONITORING PROCEDURE: Determination of Mercury Using the Flameless Atomic Absorption (Cold Vapor) Technique

Sample

Solubilization

Chemical Sample Preparation

a. Oxidation of all mercury to mercuric form
b. Reduction of all mercuric mercury to metallic mercury

Aeration

The metallic mercury is circulated as a vapor through the system

Flameless Atomic Absorption

Absorption of energy at 253.7nm from a hollow cathode lamp measurement by a photodetector

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
A. Equipment Preparation			
1. Cleaning of Glassware	1. Wash with detergent	1a. Cleaning should be carried out in this order. 1b. Care should be taken to insure clean glassware as mercury is a common contaminant. All glassware should be kept covered after cleaning.	V.A.1.1
	2. Rinse with tap water		
	3. Rinse with 1:1 Nitric Acid	3a. Add 500 ml conc. nitric acid (HNO_3) to 500 ml distilled water.	
	4. Rinse with tap water		
	5. Rinse with 1:1 Hydrochloric acid	5a. Add 500 ml conc. hydrochloric acid (HCl) to 500 ml distilled water.	
	6. Rinse with tap water		
	7. Rinse with distilled water		
2. Balance Preparation	1. Check all balances for cleanliness and proper operation.		
B. Instrumental Set-up			
1. Mercury Trap - Liquid Type	1. Before operation of the instrument, four additions to the system should be considered (Fig. I).	1a. There are two ways the flow system can be set up. It can be operated as a closed or open system. In the closed system the mercury vapor continuously passes through the system until wasted in the mercury trap by the operator. In the open system the vapor passes through the absorption tube only once and goes directly to the trap. Which system is chosen will dictate what equipment is necessary. Figure I shows the choices and the equipment necessary for each.	
	2. One of the following mercury traps should be included in the system.	2a. Because of the toxic nature of mercury vapor precaution must be taken to avoid contamination. The vapor will be held in the trap after it has been measured.	

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
1. Mercury Trap - Liquid Type (Cont'd.)	3. For a liquid type trap use a 250 ml side arm filtering flask.	3a. Use a filtering flask such as Corning #400580 or its equivalent.	
	4. Assemble as shown in Figure 2.	4a. Use a #3 cork hole borer to make the hole.	
	5. Insert straight gas dispersion tube or frit through the hole so that the bottom or fritted end is about one inch above bottom of the flask.	5a. Frit should have a course porosity such as Corning #404260 or equivalent. The frit should always fall below liquid level in the flask. Should the level become low add more liquid (Reagent #10). The nonfritted end should be lubricated and care taken when the frit is inserted through the stopper so as not to break the frit and injure the worker.	
	6. Insert into filtering flask.		
	7. Connect tygon tubing to top end of frit and a second piece of tygon tubing to the side arm of filtering flask.	7a. Care should be taken so that the liquid level does not come close to the opening of the side arm of the flask. This could flood the instrument if allowed to do so. If flooding should occur, dismantel the absorption tube and clean it and the tubing immediately.	VIII
	8. Add 200 ml of 1:1 potassium permanganate ($KMnO_4$) -- sulfuric acid (H_2SO_4) Reagent (Reagent #10)	8a. A solution of 0.25% iodine in a 3% potassium iodide (KI) solution may also be used. 8b. Filling the flask can be postponed until all of the apparatus is assembled.	
2. Mercury Trap - Solid Type	1. The apparatus can be prepared similar to the drying tube (B-3) but packed with 2-3 grams of activated carbon.	1a. Locate after 2 position valve in closed system, figure 1 (system two) or after the analyzer in an open system, figure 1 (system three).	

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
2. Mercury Trap - Solid Type (Cont'd.)	2. The equipment can be purchased with adsorbent as an option from the analyzer manufacturer.	2a. Position as above.	
3. Drying Tube	1. Construct as shown in Figure 3.	1a. Place between sample container and instrument.	
	2. Bore a hole through a number 2 stopper with a number 2 cork hole borer. Repeat with a second stopper.		
	3. Insert a 2 inch long piece of glass tubing (5 mm diameter) through each stopper allowing about 1/2 inch protruding from each end.	3a. Care should be taken when inserting glass tubing.	
	4. Fill a 6 inch piece of 3/4 inch diameter tubing with 20 grams of magnesium perchlorate ($Mg(ClO_4)_2$)	4a. Other drying agents such as calcium chloride ($CaCl_2$) may be used.	
	5. Use a small piece of glass wool in each end of the tube to prevent loss of granules.	5a. The tube should not be packed so tight as to restrict gas flow.	
	6. Insert stopper prepared above in each end of tube.		
	7. Replace drying agent when needed.	7a. Replace magnesium perchlorate or any drying agent regularly. These materials tend to cake and form a plug when their limit of saturation is approached. The length of time the material will	

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
3. Drying Tube (Cont'd.)		last will vary with use and samples. Experience will dictate a routine.	
4. Rotometer	1. Must be capable of measuring a gas flow of 1 liter per minute.	1a. Place between water trap and instrument. See Figure 1 for location. 1b. The rotometer may be removed from the circuit after the instrument pump rate is checked. 1c. The flow rate should be checked periodically to insure flow rate has not changed.	
	2. Connect one length of tubing between the sample container and the drying tube, then out of the drying tube through the rotometer to the fitting on the side of the instrument marked "in".	2a. The connection must be made to the sample container by side arm. Reverse tubing connections may flood the instrument with liquid.	
	3. A second length of tubing should begin at the fitting of the instrument marked "out" and proceed to the next piece of equipment.	3a. See Figure 1 for gas flow path.	
5. Two Position Valve	1. A two position valve is necessary when using a closed system and a trap. Use stopcock, Corning No. 442838 or equivalent for the two way valve or stopcock.		
	2. One position of the valve should go through the trap to the sample container. The other position should by-pass the trap	2a. It is important to maintain a specific air volume in the system. Once the system is calibrated this volume cannot be changed unless the system is recalibrated.	

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
5. Two Position Valve (Cont'd.)	and be connected to the fri of the sample container.		
6. MAS-50	1. Place the instrument on a flat surface where it will be isolated from shock and undue temperature variation.	1a. Do not block or cover the ventilation slots at the rear and base of the instrument.	
	2. Before turning on the instrument a check should be made of the power requirements.	2a. The instrument requires a grounded power connection. Preferably a three prong receptacle. If not then a grounded two prong set-up.	
	3. Remove back panel and note the position of the 110-220 volt switch. Place the switch in the position desired. Then close the rear panel.	3a. Should 220 V position be used an appropriate 220 V plug should be installed in place of the plug supplied with the analyzer.	
	4. Meter mechanical zero adjustment ● with power switch off ● Check to see if meter pointer indicates exactly 0 micrograms. ● Using the mechanical zero adjust screw (Figure 4). Adjust meter until it reads 0 micrograms.	4a. If meter pointer does indicate zero, no further action is necessary.	
	5. Place the On-Off switch in the On position. Allow 15 minute warm-up.		

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
6. MAS-50 (Cont'd.)	6. During warm-up check the connections in the external set-up of the gas flow path as in Figure 1.	6a. Any leaks in the system will cause low readings and allow hazardous mercury vapors to escape.	
7. Recorder (optional)	1. An external recorder may be connected to the instrument to give indications coinciding with the instruments meter.	1a. Any recorder having 50 K ohm impedance or more - the output of the instrument is vairable from 0 to 300 mV full scale. (Such as a Coleman Model 56 or 165 chart recorder)	
	2. Adjust recorder by placing instrument controls as follows: ● Meter switch - % T ● Memory - OFF ● Recorder - plugged in ● Shutter - open		
	3. Use recorder zero to align recorder with 100% T.		
	4. Use analyzer's recorder range control to achieve full scale indication on 0% T.	4a. Shutter closed for this adjustment.	
C. Reagent Preparation			
1. Sulfuric Acid 0.5 N	1. Add 14.0 ml conc. sulfuric acid (H_2SO_4) to approximately 500 ml water and mix. Then dilute with water to 1 liter volume.	1a. The concentrated H_2SO_4 should be of low mercury concentration. 1b. Unless specified the term water means distilled water.	

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
2. Potassium Permanganate Soln. 5% solution w/v	1. Prepare 100 ml of solution containing 5.0 grams potassium permanganate ($KMnO_4$)	1a. Should a larger amount of reagent solution be needed the same ratio should be maintained. For example: prepare 1000 ml of solution containing 50 grams $KMnO_4$.	
3. Potassium Persulfate Soln. 5% solution w/v	1. Dissolve 5.0 g potassium persulfate ($K_2S_2O_8$) in water and dilute to 100 ml.		
4. Sodium Chloride - Hydroxylamine Sulfate Soln. Solution 12% NaCl 12% $((HONH_2)_2 \cdot H_2SC_4)$ w/v	1. Dissolve 12.0 g of sodium chloride (NaCl) and 12.0 g of hydroxylamine sulfate ($(HONH_2)_2 \cdot H_2SO_4$) in water and dilute to 100 ml.	1a. Hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) may also be used. It should be prepared in the same manner.	
5. Stannous Sulfate soln. 10% solution w/v	1. Dissolve 25.0 g stannous sulfate ($SnSO_4$) in 0.5 N sulfuric acid and dilute with 0.5 sulfuric acid to 250 ml.	1a. Stannous chloride ($SnCl_2 \cdot 2H_2O$) may be used and be prepared in the same manner. 1b. The acid is reagent no. 1. 1c. This a suspension and should be stirred continuously during use.	
6. Sulfuric Acid Concentrated (H_2SO_4)	1. No preparation necessary.	1a. This should be reagent grade and low in mercury concentration. 1b. Caution: this is corrosive.	
7. Nitric Acid Concentrated (HNO_3)	1. No preparation necessary.	1a. This should be reagent grade and low in mercury content. 1b. Caution: this is corrosive. 1c. If a high reagent blank is obtained, it may be necessary to distill the nitric acid.	
8. Stock Mercury Soln. ($HgCl_2$) (Cont'd.)	1. Dissolve 0.1354 g of mercuric chloride ($HgCl_2$) in water.	1a. Caution: solution will increase in temperature.	

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
8. Stock Mercury Soln. ($HgCl_2$) (Cont'd.)	2. Add 10 ml conc. nitric acid (HNO_3)	2a. Concentration of stock solution is now 1 ml = 1 mg Hg	
	3. Cool to room temperature.		
	4. Dilute to 100 ml with water.		
9. Intermediate Mercury Solution - ($HgCl._2$) Dilution of Solution 8	1. This solution is a dilution of the stock solution to adjust the conc. of Hg to 10.0 µg/ml. Proceed as follows.	1a. Prepare fresh before use.	
	2. Add about 700 ml water to a 1000 ml vol. flask.		
	3. Add 0.5 ml conc. HNO_3	3a. The nitric acid conc. of the dilutions including the working solution should be maintained at 0.15%. This acid should be added to the flask before addition of the aliquot.	
	4. Add 10 ml stock Hg soln.		
	5. Dilute to 1000 ml mark. This solution contains 10 µg/ml.		
10. Working Mercury Solution - ($HgCl_2$) Dilution of Solution 9	1. Add about 700 ml water to a 1000 ml vol. flask.	1a. Prepare fresh before use.	
	2. Add 1.5 ml conc. HNO_3.		
	3. Add 10 ml of intermediate solution (10 µg/ml).		
	4. Dilute to 1000 ml mark. This is working solution and contains 0.1 µg/ml.		

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
11. Potassium Permanganate 0.1 N ($KMnO_4$) and Sulfuric Acid 10% Solution (For Mercury Trap)	1. Dissolve .316 g potassium permanganate ($KMnO_4$) in 100 ml water.	1a. Let stand until following solution is prepared.	
	2. Add 10 ml conc. sulfuric acid (H_2SO_4) to about 80 ml water. Dilute to 100 ml with water.	2a. Caution: heat generated. 2b. Should be at room temperature before volume adjustment.	
	3. Mix equal volumes of each solution; $KMNO_4$(1) and H_2SO_4 (2).		
12. Nitric Acid (1 + 1 dilution) (HNO_3)	1. Prepare by adding an equal volume of acid to an equal volume of water (i.e. 50 ml HNO_3 to 50 ml water).	1a. Caution: acid should always be added to water to avoid spattering. 1b. Caution: Heat is generated. 1c. Use safety glasses.	
13. Hydrochloric Acid (1 + 1 dilution HNO_3)	1. Prepare by adding an equal volume of acid to an equal volume of water (i.e. 50 ml HCl to 50 ml water).	1a. See cautions above. 1b. Use safety glasses.	
D. Sample Handling and Preservation	1. Upon collection the sample pH should be lowered to 2 or lower by the addition of concentrated nitric acid.	1a. If only dissolved mercury is to be determined the sample should be filtered before addition of the acid. For total mercury the filtration is omitted.	

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
E. Solubilization of Sample	1. Acidify the sample with 1:1 nitric acid to a pH of 2 at the time of sample collection.		
	2. Transfer 100 ml of well mixed sample to a 150 ml beaker.	2a. 100 ml is the usual sample volume. If more metals are to be determined, a larger sample volume must be used.	
	3. Add 3 ml of concentrated nitric acid to the sample.	3a. Use a 10 ml graduated pipet.	
	4. Place the beaker on a hot plate and cautiously evaporate to dryness.	4a. The sample should not boil during this time.	
	5. Cool the beaker and add another 3 ml portion of the concentrated nitric acid.	5a. Use a 10 ml graduated pipet.	
	6. Cover the beaker with a watch glass and return to the hot plate.		
	7. Increase the temperature of the hot plate so that a gentle reflux action occurs.	7a. This will be indicated by droplets forming on the underside of the watch glass.	
	8. Continue heating until a light colored residue forms.	8a. This will indicate that the digestion is complete.	

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
E. Solubilization of Sample (Continued)	9. Add sufficient [1:1 hydrochloric acid (HCl) solution] and again warm the beaker to dissolve the residue.	9a. Use a 1 ml graduated pipet.	
	10. Wash down the beaker walls and watch glass with distilled water.		
	11. Adjust the volume to 100 ml (or the starting volume size).	11a. The sample is now ready for analysis.	
F. Calibration	1. Turn on power and pump switches.	1a. Refer to figure 4 and 5. 1b. Allow 15 minutes warm-up time. 1c. Calibration is necessary initially and thereafter only if mercury lamp or optical filter is replaced or if readings with standard samples constantly deviate more than 5% of full-scale in one direction.	
	2. Set range switch on %T.	2a. Refer to Figure 5 for location of various switches.	
	3. Memory switch off.		
	4. Shutter closed.		
	5. Adjust to 0%T with 0%T adjustment knob.		

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
F. Calibration (Cont'd.)	6. Open shutter.		
	7. Adjust 100% T with 100% T adjustment knob.		
	8. Repeat steps 4 through 7 until 0% T adjustment does not change full-scale (100% T) setting.		
	9. Prepare four samples of 100 ml volume containing 1.0 µg of mercury.	9a. Use the working solution (Reagent #10) (0.1 µg/ml). and dilute 10 ml of that solution to 100 ml with distilled water. This 100 ml volume will now contain 1.0 µg Hg.	
	10. Place the meter switch on % T and open shutter, memory switch off, check 0% T and 100% T settings.	10a. This step should be performed just after placing the aerator in the sample BOD bottle.	
	11. Determine as if these four standards were samples. Record the % T value for each standard sample.	11a. Use steps 18-32 of Section F - Sample Determination. 11b. When the sample contains only distilled water and an inorganic mercury (i.e., mercuric chloride) the heating step (steps 23 and 24 of sample determination) can be omitted.	
	12. Adjust meter switch to X1.	12a. This step should only be done after the needle of the meter has returned to 100% T.	
	13. Adjust the 100% T knob so that meter indicates value of mercury standard.	13a. The meter should be adjusted on the X1 setting to read 1 mg on the X1 scale.	
	14. Set meter switch to % T.		

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
F. Calibration (Cont'd.)	15. Using the calibration adjust % T to average value found in step 11.	15a. Located on the back of the analyzer. This is a screwdriver adjustment.	
	16. Switch meter switch between X1 and % T settings.	16a. The two scales should agree on the location of the needle. The X1 scale showing 1 μg and the % T scale showing 55% T (the corresponding % T value just below 1 μg on the X1 scale).	
	17. Reset 0% T and 100% T with meter switch at % T and memory off.		
	18. Transfer 0, 0.5, 1.0, 2.0, 5.0, and 10 ml portions of the working mercury solution (sol. 10) to a series of 300 ml BOD bottles.	18a. Working solution contains 0.1 μg per ml. The series will contain from 0 to 1.0 μg of mercury.	
	19. Add enough water to each bottle to make a total volume of 100 ml.	19a. The 0 μg or blank is a check on the purity of the reagents.	
	0. Treat as samples using the procedure under sample determination.		
	1. Construct a standard curve.	21a. Use arithmetic graph paper and plot maximum meter reading versus micrograms of mercury in standard.	II.E.21a
G. Sample Determination Operation	1. Plug the line cord into power receptacle.	1a. This procedure provides start-to-shutdown instructions. It is assumed that the analyzer is properly installed (Instrument Set-Up) adjusted, and calibrated (Calibration).	

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
G. Sample Determination Operation (Cont'd.)	2. Allow at least 15 minute warm-up.		
	3. Memory switch OFF.		
	4. Meter switch to % T.		
	5. Close shutter.		
	6. Turn 0% T knob to adjust meter pointer to approximately 0% T.		
	7. Open shutter.		
	8. Turn 100% T knob to adjust meter pointer to exactly 100% T.		
	9. Close shutter.		
	0. Readjust 0% T.		
	1. Open shutter.		
	2. Meter switch to X5.		
	3. Adjust 100% T.		
	4. Depress reset button.	14a. This step is necessary only on older model instruments.	
	5. Set memory switch as desired.	15a. With memory switch on, the meter will hold the maximum value. At the OFF position the analyst will have to watch for the highest value. The memory switch must be turned off after each run to cancel the meter reading and allow instrument	

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
G. Sample Determination Operation (Cont'd.)		to return to zero. In all cases the memory function does not affect the recorder.	
	16. Select desired scale - X1, X5, % T.	16a. Scale X1 - Direct reading 0 to 9 µg of Hg X5 - Direct reading 0 to 0.28 µg of Hg % T - Energy transmission scale 100 to 0% T.	
	17. Pour 100 ml of sample into BOD bottle.	17a. If the sample has more than 9 µg of mercury a smaller portion of sample should be used and diluted to 100 ml. The resulting value should be multiplied by the dilution factor. 17b. Use a separate BOD bottle for each sample or standard. The reagents can be added to the bottle and bottles can be heated.	VII 17.
	18. Add 5 ml conc. sulfuric acid (H_2SO_4). Mix.	18a. Use caution when adding concentrated acids.	
	19. Add 2.5 ml conc. nitric acid (HNO_3). Mix.		
	20. Add 15 ml potassium permanganate ($KMnO_4$) - reagent no. 2.	20a. Shake and add additional portions of potassium permanganate solution, if necessary, until the purple color persists for at least 15 minutes. 20b. A small (25 ml) graduated cylinder can be used.	
	21. Allow to stand 15 minutes.	21a. This is a standing time and the sample should be allowed to actually stand for the 15 minutes.	
	22. Add 8 ml potassium persulfate ($K_2S_2O_8$) - reagent no. 3.		
	23. Heat in a water bath at 95°C for 2 hours.	23a. The heat step is required for methyl mercuric chloride when present in or spiked to a natural system. For standards prepared with distilled water and mercuirc chloride, the heating step is not necessary.	

EFFLUENT MONITORING PROCEDURE: Determination of Mercury Using the Flameless Atomic Absorption (Cold Vapor) Technique

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
G. Sample Determination Operation (Cont'd.)	24. Cool to room temperature.	24a. Tap water can be used to adjust this temperature.	
	25. Add 6 ml of sodium chloride, hydroxylamine sulfate, ($NaCl-(HONH_2)_2 \cdot H_2SO_4$) reagent no. 4.	25a. This is done to reduce the excess potassium permanganate.	
	26. Allow to stand at least 30 seconds.	26a. Up to this point all samples to be run could be treated together as a group. From this point each must be done individually as the mercury is generated and must be measured immediately.	
	27. Add 5 ml of stannous sulfate ($SnSO_4$) solution. reagent no. 5.		
	28. Immediately insert bubbler into the bottle.	28a. The shutter should be open and the valve in the position to by-pass the trap.	
	29. Record the highest value indicated by the meter pointer.	29a. The meter will increase and reach a maximum within 1 minute. 29b. With the memory switch on, the meter will automatically retain the highest value reached. 29c. With the memory switch off, either a recorder must be used or the meter watched continuously.	
	30. In the closed system, turn one stopcock valve to the trap position and allow pump to continue operating.	30a. Once this has been done the mercury will be absorbed and the sample cannot be reused.	
	31. Position memory to OFF if it was used.	31a. On new instruments this will clear memory. On older instruments the reset button should be depressed. 31b. Before the next sample can be started the meter must be returned to the o µg position.	

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
G. Sample Determination Operation (Cont'd.)	32. Turn stopcock valve to the sample position.		
	33. Remove frit from sample container.	33a. Pump should be allowed to continue operating.	
	34. Determine all other samples by repeating steps 7 through 31.		
	35. When last sample has run, shut down analyzer.	35a. To shut down, keep valve to trap until meter reads 0%, and then remove aerator from BOD bottle. It is recommended that the analyzer be left ON during the day if routine sampling is to continue.	
H. Calculations	1. Use values determined from the standards.	1a. Step 20 under Calibration.	
	2. Plot the meter reading (μg) versus the known concentration of the standards (μg).	2a. This will show if the meter is in calibration. If all readings agree, i.e., if for example, a known standard of 1.0 μg concentration reads 1.0 μg on the X1 scale, the unknown sample concentrations can be read directly in μg. Otherwise the standard curve should be used to obtain the correct value.	
	3. Calculate the mercury concentration in the sample.	3a. Use the equation: $\mu g\ Hg^{*}/l = \left(\begin{matrix}\mu g\ reading\\ from\ meter\end{matrix}\right) \times \left(\frac{1000}{ml's\ of\ sample\ used}\right)$ *Hg = Mercury	

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
H. Calculations (Cont'd.)	4. Report mercury conc. as follows: Below 0.2 µg/l as <0.2 µg/l Between 1.0 and 10.0 µg/l using one place after decimal Above 10.0 µg/l using only whole numbers	4a. < = less than.	

TRAINING GUIDE NOTE	REFERENCES/RESOURCES
Theoretical Concepts	
The method is based on the method developed by Hatch and Ott. The Mercury in the sample is oxidized to the mercuric ion with potassium permanganate in a nitric-sulfuric acid medium. Hydroxylamine sulfate is then added to remove the excess permanganate. Stannous sulfate, is then added to reduce the mercury to metallic form. Then the mercury is vaporized and circulated by the bubbler system. This consists of a circulating pump and the bubbler. Measurement is made with a flameless atomic absorption spectrophotometer. The energy at the 253.7 nm mercury line emitted by a mercury lamp is absorbed by the mercury vapor in the flow-through absorption cell. The change in transmittance is detected by a phototube.	Analytical Chemistry, Volume 40, pg. 2085 December 1968 Instruction Manual Coleman Model MAS-50 Mercury Analyzer Coleman Instruments Maywood, IL

TRAINING GUIDE NOTE

REFERENCES/RESOURCES

E.21.A

The standard curve is a reference to a fundamental law of absorption chemistry known as the Beer-Lambert law. Simply, this law states that the amount of energy absorbed by a solution is proportional to the concentration of the absorbing material in the solution. Applied to this outline the amount of energy absorbed at the wavelength of 253.7 nm is proportional to the amount of mercury present in a solution.

If a series of known solutions are prepared as in step 18 under Calibration and the meter reading, i.e. the maximum reading on either the % T or the X1 scale are plotted, a straight line should result.

When an unknown sample value is obtained its mercury content can be determined from the straight line or standard curve.

The two meter setting, i.e., % T and X1 will give the same reuslts. Percent T will require a standard curve to convert the % T reading to concentration while the X1 scale will convert and express the reading directly into micrograms of mercury.

To use the attached graph paper prepare the standards as in step 18 and 19 of the Calibration section and run them as samples. The known concentrations are plotted along the bottom of the graph. Then plot the values obtained from the meter, X1 is plotted on the left of the graph and % T is plotted on the right.

Where the known concentration line intersects with the appropriate meter reading a mark is made. After all six standards are plotted, draw a line through the marks.

	TRAINING GUIDE NOTE	REFERENCES/RESOURCES
A.1.1	The use of chromic acid is a recommended procedure.	
	1. Pour 35 ml of distilled water in a 250 ml beaker.	13th Standard Methods, p. 135, section 2.c.2
	2. Add about 1/8 teaspoon (simply estimate this quantity) of sodium dichromate, $Na_2Cr_2O_7$, to the water.	
	3. Swirl the beaker until the sodium dichromate has dissolved.	
	4. Keep repeating steps 2 and 3 until no more sodium dichromate will dissolve.	
	5. Pour the solution into a 2 liter beaker.	
	6. Slowly pour 1 liter of concentrated sulfuric acid, H_2SO_4, into the 2 liter beaker. Caution: Use eyeglasses and protective clothing.	
	7. Stir the mixture thoroughly.	
	8. Store it in a glass stoppered bottle.	
	9. The cleaning solution should be at a temperature of about 50°C when it is used.	
	10. It may therefore be necessary to warm the cleaning solution.	
	11. When using the warm cleaning solution, fill the piece of glassware with the solution.	
	12. Allow it to soak for 2-3 minutes (or longer).	
	13. Pour the cleaning solution back into the storage bottle.	
	14. Rinse the piece of glassware ten times with tap water.	
	15. The cleaning solution may be reused until it turns green.	
	16. It should then be discarded.	

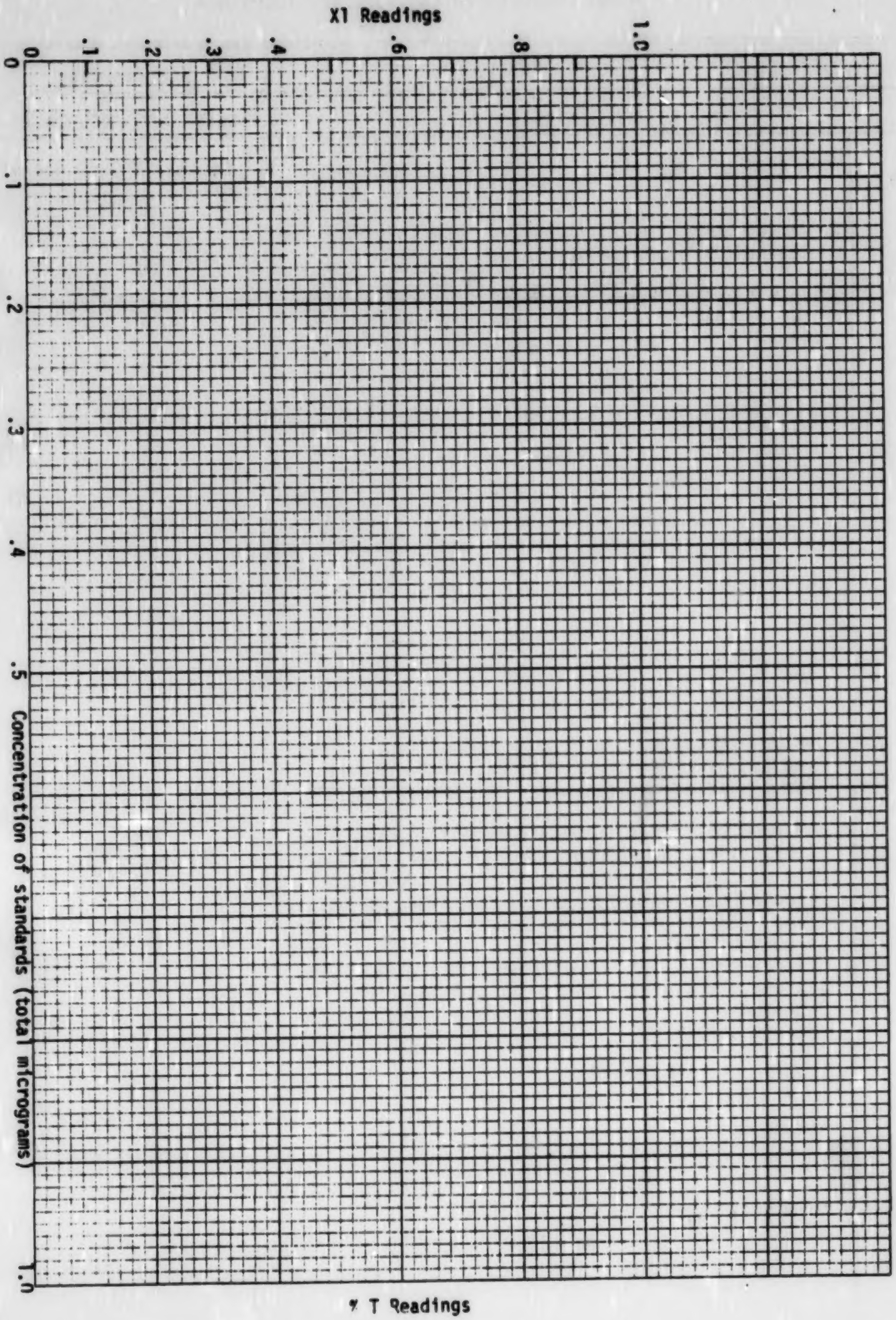
TRAINING GUIDE NOTE

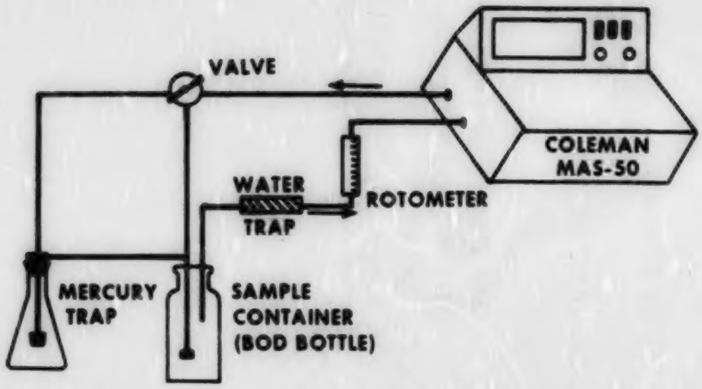
Maintenance Practices

1. Immediately clean all spilled materials from the instrument and wipe dry.
2. Do not leave vapors in absorption cell. Remove bubbler from the sample flask and operate pump after passing air through trap for 2 minutes.
3. Whenever the instrument is not in relatively continuous use, turn it off and cover it with the plastic cover. If it is not to be used for several days, the line cord may be disconnected from the power source.
4. Circulating air may eventually cause dust to accumulate on exposed optical parts. Parts, such as the lamp filter and cell windows may be wiped with clean, lintless, non-scratching tissue.
5. If a liquid sample should be drawn into the Analyzer disconnect the tubing at both ends of the absorption tube. Remove the tube, disassemble, rinse with distilled water, dry and reassemble with new windows. Flush the system with distilled water introduced at the cell end of both inlet and outlet tubing. Then gently blow out both lines with air. Re-install the absorption cell.
6. If problems arise in attaining either 0% T or 100% T with the appropriate adjustment controls, the windows in the absorption tube should be checked particularly the one opposite the mercury lamp. If the cell window has become cloudy it should be changed. Care should be taken to keep finger prints off the windows. After exposure to the ultra-violet light the prints cannot be removed. To replace follow the manufacturer's directions.

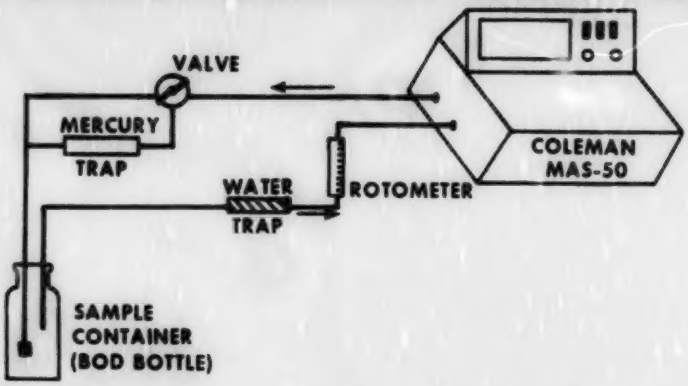
REFERENCES/RESOURCES

Coleman MAS-50 Operation Manual

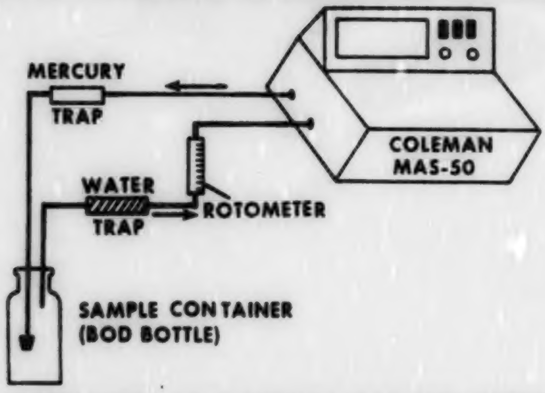

X1 Readings
0
.1
.2
.3
.4
.6
.8
1.0
0
.1
.2
.3
.4
.5
Concentration of standards (total micrograms)
1.0
% T Readings


VALVE
COLEMAN
MAS-50
WATER
TRAP
ROTOMETER
MERCURY
TRAP
SAMPLE
CONTAINER
(BOD BOTTLE)

SYSTEM ONE: LIQUID MERCURY TRAP CLOSED SYSTEM


VALVE
MERCURY
TRAP
COLEMAN
MAS-50
WATER
TRAP
ROTOMETER
SAMPLE
CONTAINER
(BOD BOTTLE)

SYSTEM TWO: SOLID MERCURY TRAP CLOSED SYSTEM


MERCURY
TRAP
COLEMAN
MAS-50
WATER
TRAP
ROTOMETER
SAMPLE CONTAINER
(BOD BOTTLE)

SYSTEM THREE: SOLID MERCURY TRAP OPEN SYSTEM

Figure 1. FLOW SYSTEMS FOR THE COLD VAPOR TECHNIQUE FOR MERCURY

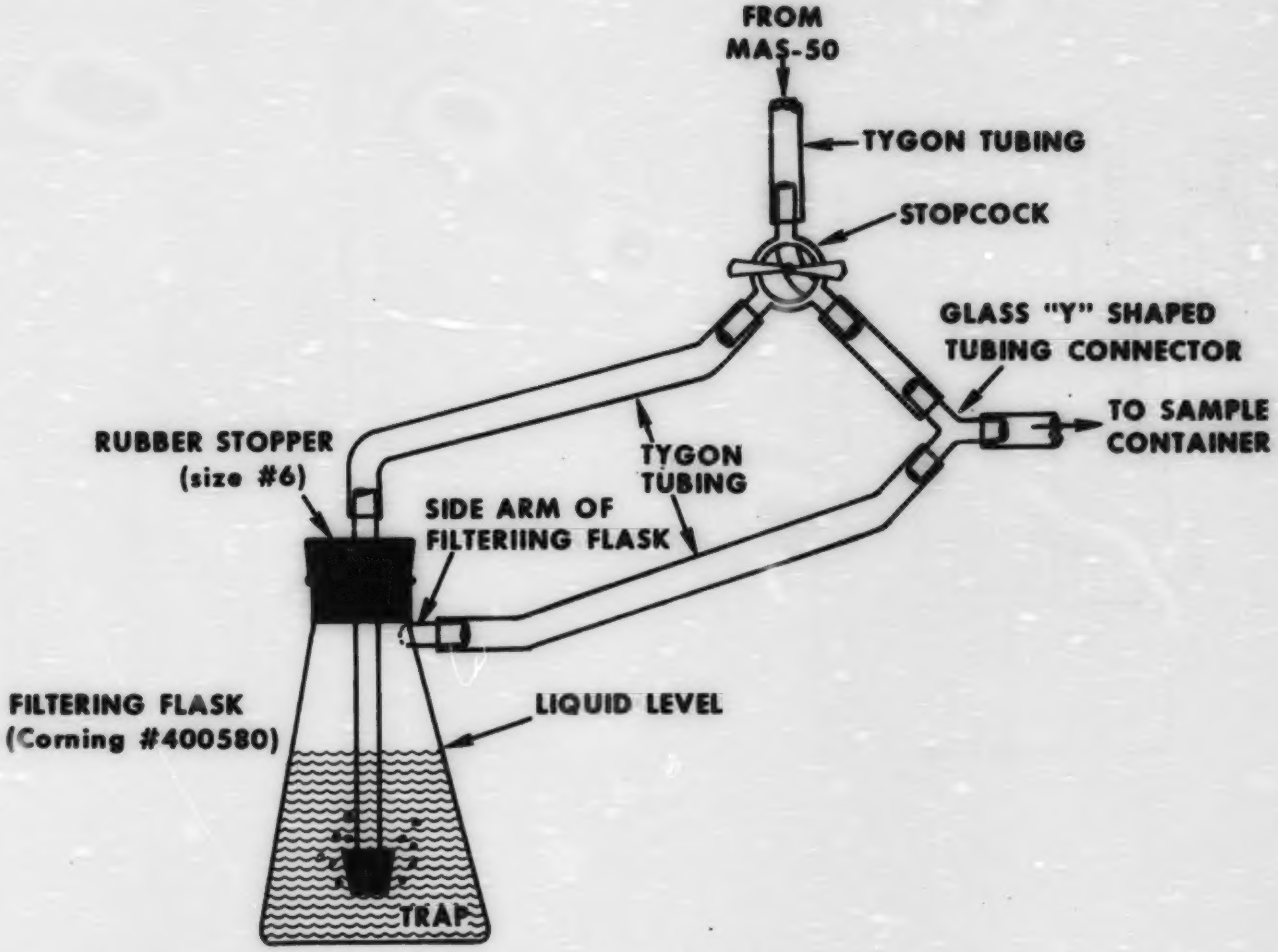

FROM MAS-50
TYGON TUBING
STOPCOCK
GLASS "Y" SHAPED TUBING CONNECTOR
TO SAMPLE CONTAINER
RUBBER STOPPER (size #6)
TYGON TUBING
SIDE ARM OF FILTERIING FLASK
FILTERING FLASK (Corning #400580)
LIQUID LEVEL
TRAP

Figure 2. ARRANGEMENT OF TWO-POSITION STOPCOCK AND MERCURY TRAP

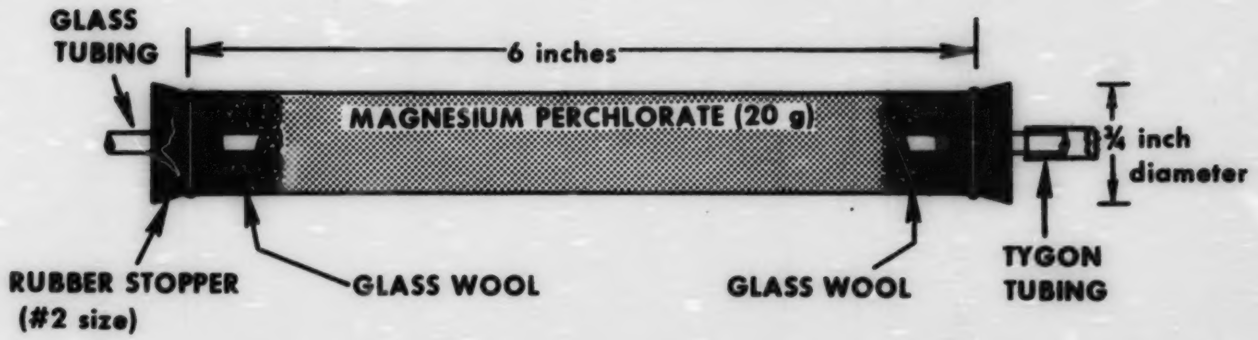

GLASS TUBING
6 inches
MAGNESIUM PERCHLORATE (20 g)
¾ inch diameter
RUBBER STOPPER (#2 size)
GLASS WOOL
GLASS WOOL
TYGON TUBING

Figure 3. DRYING TUBE

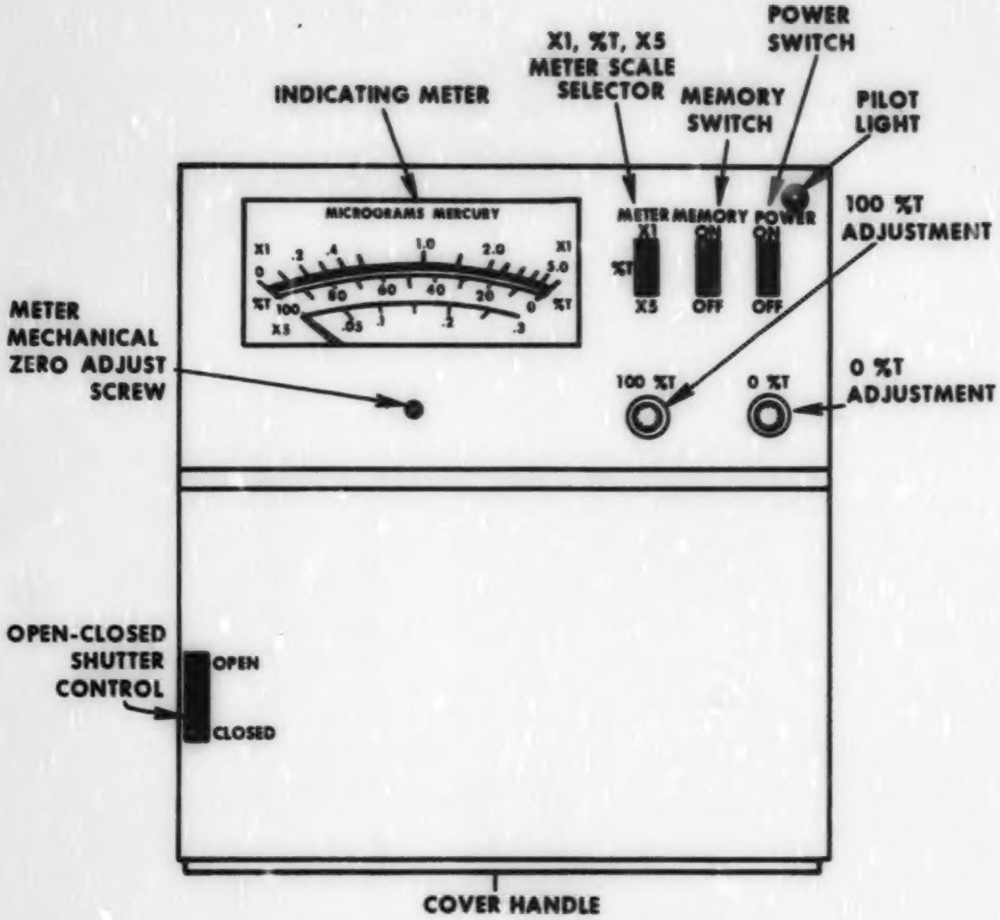

POWER SWITCH
X1, %T, X5 METER SCALE SELECTOR
INDICATING METER
MEMORY SWITCH
PILOT LIGHT
MICROGRAMS MERCURY
METER
X1
%T
X5
MEMORY
ON
OFF
POWER
ON
OFF
100 %T ADJUSTMENT
METER MECHANICAL ZERO ADJUST SCREW
100 %T
0 %T
0 %T ADJUSTMENT
OPEN-CLOSED SHUTTER CONTROL
OPEN
CLOSED
COVER HANDLE

Figure 4. FRONT CONTROLS AND OPERATIONAL COMPONENTS

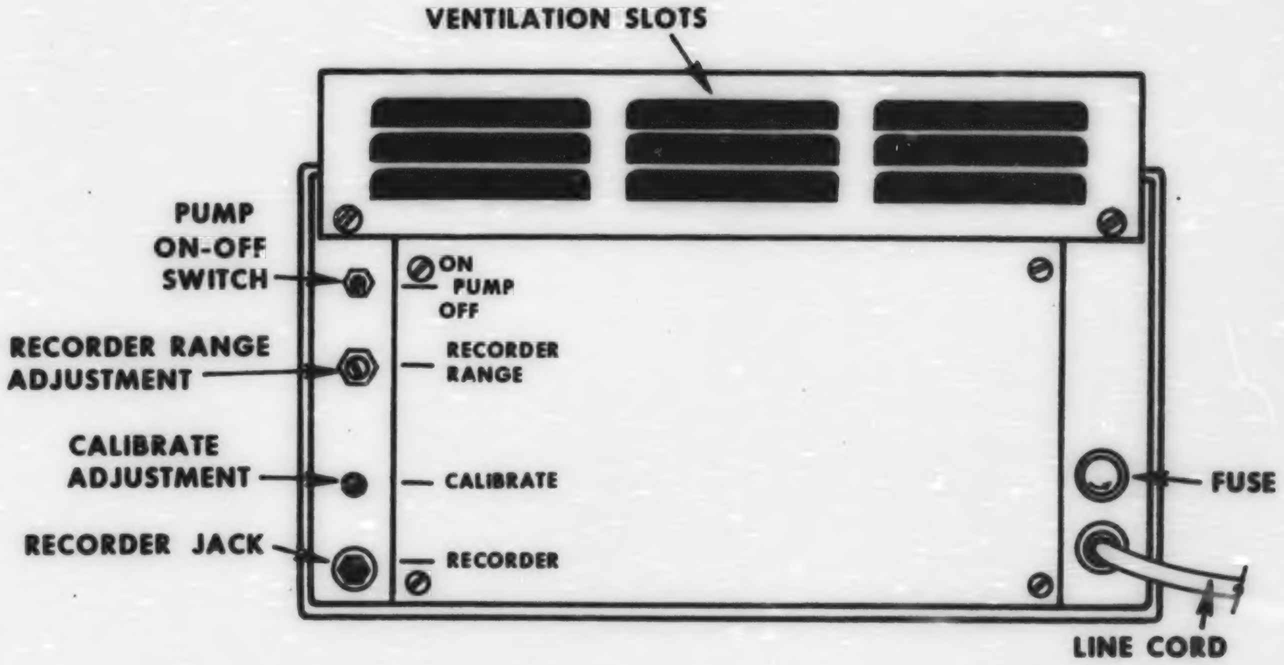

VENTILATION SLOTS
PUMP ON-OFF SWITCH
RECORDER RANGE ADJUSTMENT
CALIBRATE ADJUSTMENT
RECORDER JACK
ON PUMP OFF
RECORDER RANGE
CALIBRATE
RECORDER
FUSE
LINE CORD

Figure 5. REAR PANEL

A PROTOTYPE FOR DEVELOPMENT OF ROUTINE OPERATIONAL PROCEDURES

for the

DETERMINATION OF POTASSIUM USING FLAME PHOTOMETRY

as applied in

WASTEWATER TREATMENT FACILITIES
and in the
MONITORING OF EFFLUENT WASTEWATERS

Developed by the

National Training and Operational Technology Center
Municipal Operations and Training Division
Office of Water Program Operations
U.S. Environmental Protection Agency

EFFLUENT MONITORING PROCEDURE: Determination of Potassium Using Flame Photometry

This operational procedure was developed by:

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ADDRESS EPA, OWPO, NTOTC, Cincinnati, Ohio 45268

POSITION Chemist-Instructor

EDUCATION AND TECHNICAL BACKGROUND

B.S. - Chemistry

M.S. - Chemistry

1-1/2 years Industrial Chemist

4 years additional Graduate School

4 years College Chemistry Instructor

1-1/2 years DHEW - Air Pollution Program, Chemist

10 years DI - EPA, Chemist-Instructor

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EFFLUENT MONITORING PROCEDURE: Determination of Potassium Using Flame Photometry

1. Analysis Objectives:

   The learner will determine the potassium content of a sewage effluent.

2. Brief Description of Analysis:

   The learner will prepare a calibration graph using the percent transmittance and the concentration of a series of standard potassium solutions. The percent transmittance of a sample of sewage effluent will next be determined, and the potassium concentration found by using the calibration graph.

   The work will be done using a Beckman Model B spectrophotometer with flame photometry attachments. Although this procedure has been prepared for use with a specific instrument, other equivalent commercially available instruments may of course be used. Mention of a particular brand name does not constitute endorsement by the U.S. Environmental Protection Agency.

3. Applicability of this Procedure:

   a. Range of Concentration:

      Concentration levels as low as 0.1 mg/liter can be detected in a good flame photometer. Although the cited reference (below) does not specifically state the highest potassium concentration which may be determined, a limit of 10 mg/liter may be inferred. Therefore, sample dilution may be required.

   b. Pretreatment of Samples:

      The digestion procedure referenced in the Federal Register, Wednesday, December 1, 1976, Part II, table I, footnote 15 (Methods for Chemical Analysis of Water & Wastes, 1974, page 83, par. 4.1.4.) is given in this effluent monitoring procedure.

   c. Treatment of Interferences in the Sample:

      When the following ratios are exceeded, an interference in the determination of potassium is present, and the cited reference must be consulted.

Ratio	Value of the Ratio
sodium/potassium	5/1
calcium/potassium	10/1
magnesium/potassium	100/1

This procedure was taken from the Standard Methods, 14th ed., pg. 234, Method 317 A, and from the Beckman Instrument Manual.

EFFLUENT MONITORING PROCEDURE: Determination of Potassium Using Flame Photometry

Equipment and Supply Requirements

A. Capital Equipment:

1. Beckman Model B. spectrophotometer with flame photometer attachments and instrument manual
2. Source of distilled water
3. Source of deionized water
4. Oven, for use at 110°C and at 103°C (the oven used in the sodium procedure CH.MET.es.EMP.1b.7.77, Determination of Sodium Using Flame Photometry, may be used here)
5. Analytical balance, 100 g capacity

B. Reusable Supplies:

1. Trip balance, 100 g capacity
2. Pencil or pen
3. Twelve inch ruler
4. Graduated cylinder, 50 ml (for glassware cleaning)
5. Beaker, 150 ml
6. Beaker, 250 ml (for glassware cleaning)
7. Beaker, 2 liter (for glassware cleaning)
8. Laboratory apron
9. Safety glasses
10. Glass stoppered bottle, 1 liter (for storage of cleaning solution)
11. Three polyethylene bottles, 200 ml
12. One or two polyethylene bottles, 1 liter. (See page 6-13, steps 9 and 10.)
13. Graduated cylinder, 250 ml
14. Erlenmeyer flask, 125 ml
15. Erlenmeyer flask, 500 ml
16. Graduated cylinder, 100 ml
17. Graduated cylinder, 10 ml
18. Plastic weighing boat, about 2 inches square
19. Small spatula
20. One or two volumetric flasks, 1 liter (See page 6-13, 9a.)
21. Pipet, 100 ml
22. Two plastic squeeze bottles
23. Funnel, about 60 mm diameter
24. One piece Whatman number 40 (or equivalent) filter paper (to fit the funnel)
25. One ring (to support the funnel)
26. Six, or twelve, volumetric flasks, 100 ml (See page 6-17, 3a.)
27. One pipet bulb
28. One or two graduated pipets, 10 ml (See page 6-17, 3a.)
29. Eight, or sixteen, small beakers (depending on whether one or both sets of standards are prepared); either glass (supplied with the flame photometer) or disposable plastic, and used to hold solutions for aspiration
30. Two pressure regulators (one for hydrogen, one for oxygen)
31. Wrenches for use in attaching pressure regulators to gas cylinders
32. Wrench for use in making hose connections
33. Two clamps (for safely anchoring gas cylinders)
34. Screwdriver, medium size
35. One ring stand
36. Hot plate

B. Reusable Supplies (Continued)

37. Thermometer, 100°C
38. One piece of rubber or plastic tubing to fit onto the tube extending from the bottom of the atomizer burner, 1 ft.
39. Asbestos gloves or crucible tongs
40. One piece of pH sensitive paper (to measure a pH of 2)

C. Consumable Supplies:

1. Potassium chloride, KCl, 3 g.
2. One piece graph paper; divided into squares of equal size
3. Sodium dichromate, $Na_2Cr_2O_7$ (for cleaning glassware)
4. Concentrated sulfuric acid, H_2SO_4 (for cleaning glassware)
5. Soap (for cleaning glassware)
6. Brush (for cleaning glassware)
7. Brush (for cleaning balance)
8. Paper towels
9. Matches
10. Concentrated nitric acid, HNO_3
11. Cylinder of hydrogen gas (for use with the flame photometer)
12. Cylinder of oxygen gas (for use with the flame photometer)
13. Concentrated hydrochloric acid, HCl
14. Distilled concentrated nitric acid, HNO_3*

All reagents should be of high quality. Different chemical manufacturers may have different ways of indicating a high quality reagent. While no endorsement of one chemical manufacturer over another is intended, the following are some designations used in four chemical catalogs to indicate high quality reagents.

Catalog	Designations
Thomas	Reagent, ACS, Chemically (Pure (CP)
Matheson, Coleman & Bell	Reagent, ACS
Curtin Matheson Scientific, Inc.	Primary Standard, ACS, AR
Fisher	Certified, ACS

* This reagent is used for acidifying the sample at the time of collection. It must be of higher purity than Reagent, ACS, etc. J. T. Baker "Ultrex" nitric acid is an example of a higher purity acid.

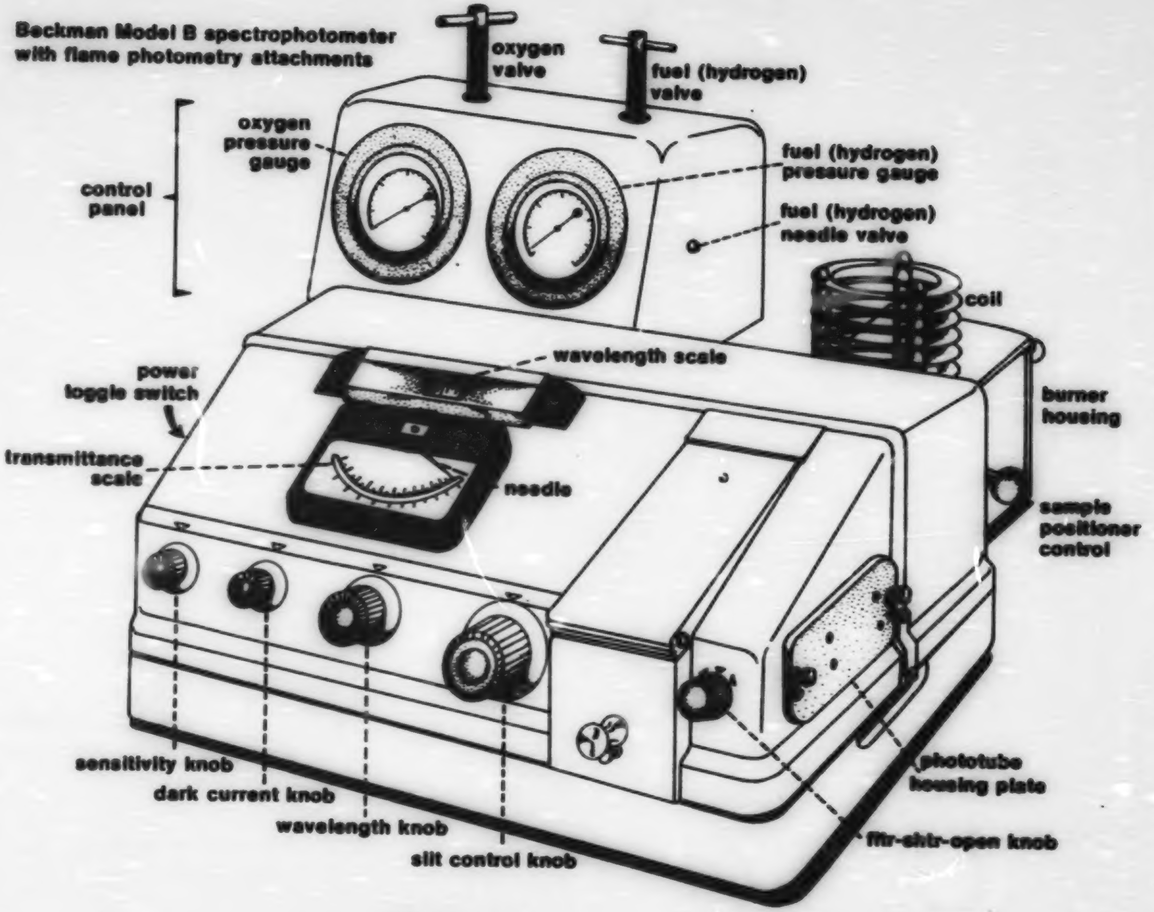
Beckman Model B spectrophotometer
with flame photometry attachments
oxygen valve
fuel (hydrogen) valve
control panel
oxygen pressure gauge
fuel (hydrogen) pressure gauge
fuel (hydrogen) needle valve
coil
wavelength scale
power toggle switch
burner housing
transmittance scale
needle
sample positioner control
sensitivity knob
dark current knob
wavelength knob
slit control knob
phototube housing plate
fltr-shtr-open knob

Figure 1

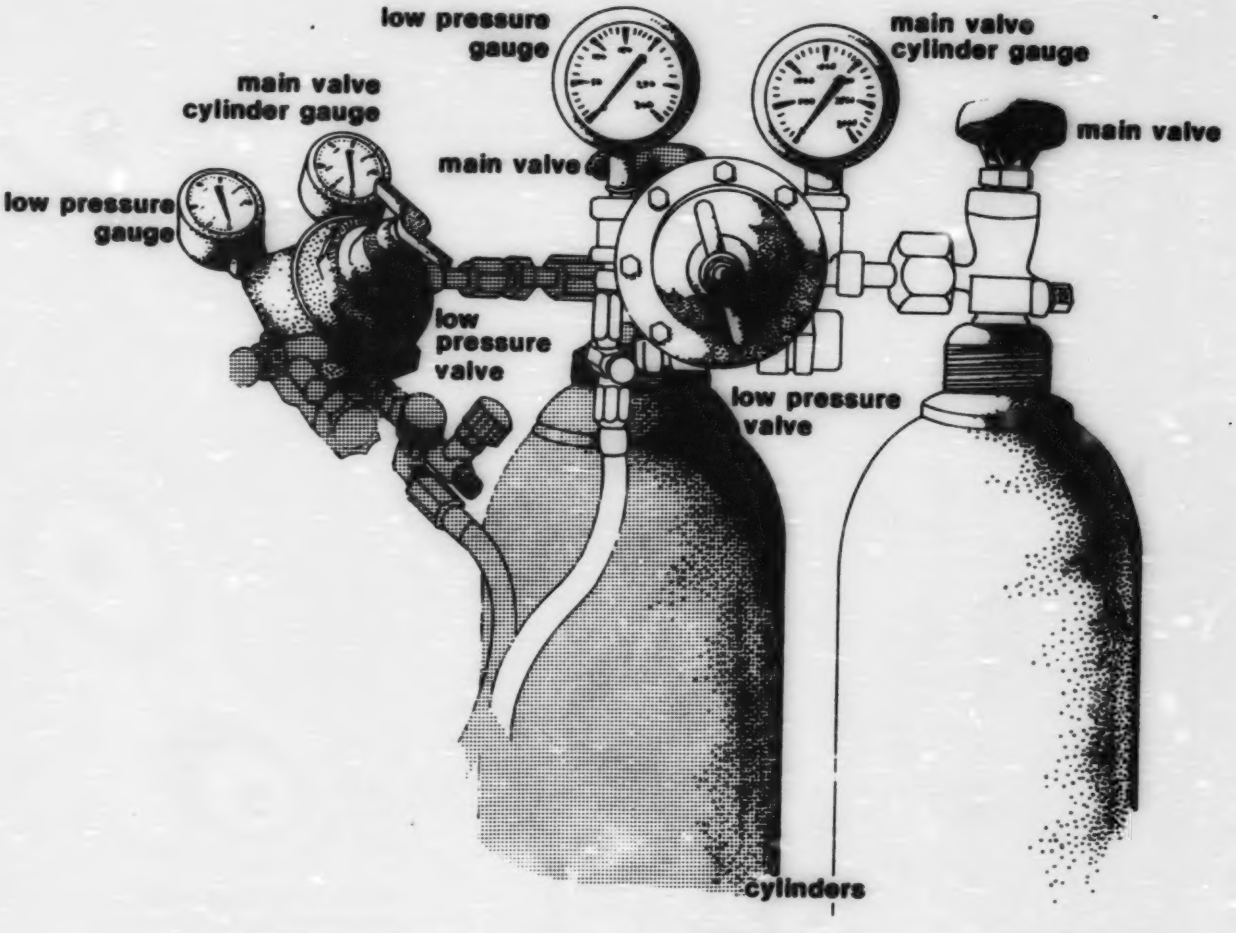
low pressure gauge
main valve cylinder gauge
low pressure gauge
main valve
main valve cylinder gauge
main valve
low pressure valve
low pressure valve
cylinders

Figure 2

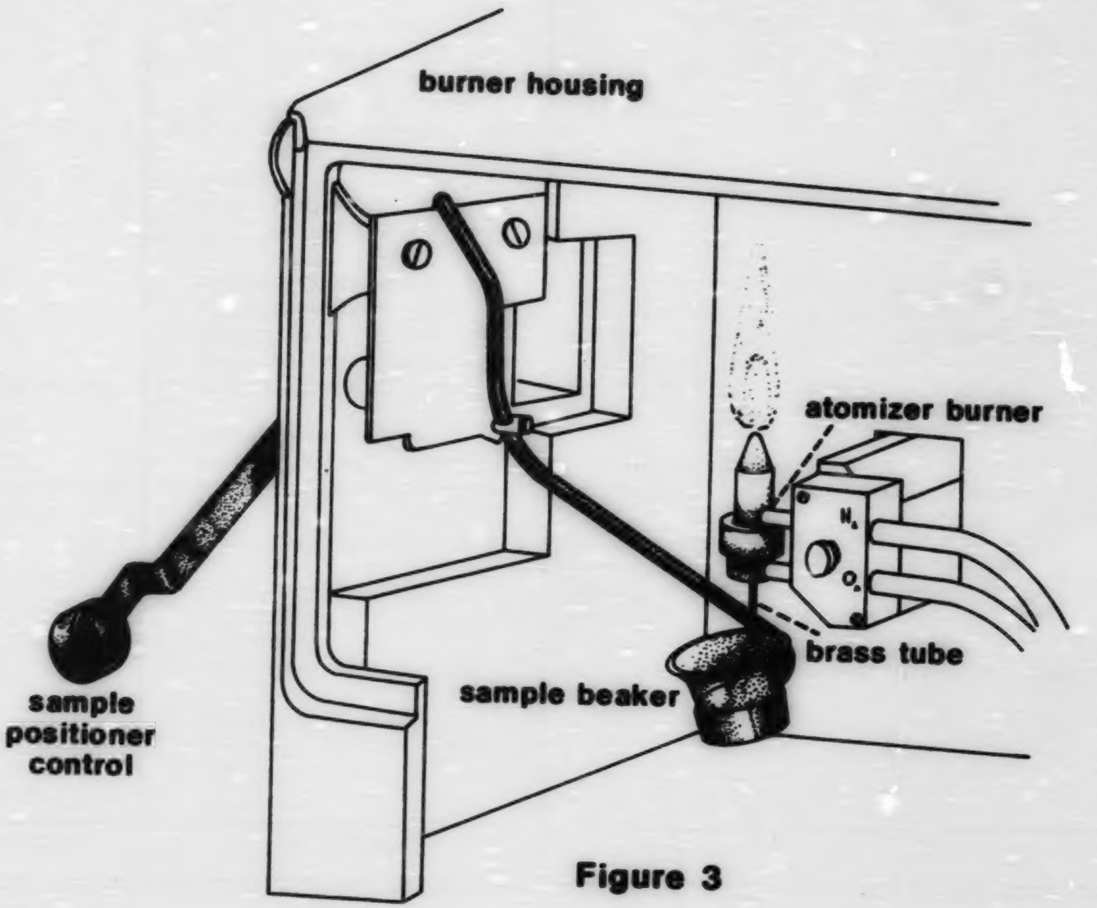
burner housing
atomizer burner
N_2
O_2
brass tube
sample beaker
sample positioner control

Figure 3

EFFLUENT MONITORING PROCEDURE: Determination of Potassium Using Flame Photometry

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
A. Equipment Preparation			V.A.1.1
1. Cleaning of Glassware	1. Clean all glassware and polyethylene bottles.		
	2. Rinse with nitric acid solution.	2a. Preparation of the acid is described in B.1.	
	3. Rinse with tap water.	3a. Ten times.	
	4. Rinse with deionized water.	4a. Five times.	
2. Balance Preparation	1. Check the analytical balance for cleanliness and proper operation.	1a. Consult the manufacturer's manual if the balance does not operate properly.	
3. Spectrophotometer	1. Attach the oxygen and hydrogen cylinders to the Beckman Model B spectrophotometer with flame photometry attachments.	1a. Consult the manufacturer's manual for specific instructions. 1b. For the remainder of this procedure, the words instrument, or flame photometer, will be used to mean this particular instrument.	
	2. Turn the wavelength knob to a reading of 760 nanometers.		
	3. Turn the slit control knob to a reading of 0.4 mm.		
	4. Turn the sensitivity knob to the standby position.		
	5. Turn the fltr-shtr-open knob to the shtr position.	5a. This is the closed position.	

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
A. Equipment Preparation (Continued)			
4. Phototube	1. Remove the phototube housing plate (see Figure 1).	1a. The red sensitive phototube should be used for potassium determination. 1b. Refer to figures 1, 2, & 3 when other parts of the instrument are mentioned in this procedure.	
	2. Check the condition of the desiccant in the phototube compartment.	2a. It may need drying at 103-105°C for 1 hour, followed by cooling in a desiccator for 30 min. 2b. The spectrophotometer will be turned on in E.	
B. Reagent Preparation			
1. Nitric Acid, HNO_3, Solution, 1 + 15	1. Measure 150 ml of distilled water.	1a. Use a 250 ml graduated cylinder.	
	2. Pour it into a 500 ml Erlenmeyer flask.		
	3. Measure 10 ml of concentrated nitric acid, HNO_3.	3a. Use a 10 ml graduated cylinder.	
	4. Pour the nitric acid slowly into the distilled water.		
	5. Swirl the flask.	5a. To mix the acid and water.	
	6. Store the solution in a polyethylene bottle.	6a. This solution is used for rinsing glassware and polyethylene bottles. 6b. Larger amounts may be prepared using the same proportion of acid and water.	

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
B. Reagent Preparation (continued)			
2. Nitric Acid, HNO_3, Distilled	1. See 1a.	1a. This reagent is used undiluted for acidifying the sample at the time of collection.	
3. Hydrochloric Acid, HCl, Distilled, 1 + 1	1. Measure 2.5 ml of distilled hydrochloric acid, HCl.	1a. Use a 10 ml graduated cylinder. 1b. Five ml of the 1 + 1 mixture are needed for each sample. Therefore, larger volumes may be prepared as necessary.	
	2. Pour it into a 125 ml Erlenmeyer flask.	2a. Use a larger flask if larger amounts of the mixture are being prepared.	
	3. Measure 2.5 ml of deionized water.	3a. Use the 10 ml graduated cylinder from 1a.	
	4. Pour it into the same flask.		
	5. Swirl the flask.	5a. To mix the acid and water.	
	6. Store the solution in a polyethylene bottle.		
4. Stock Potassium Solution	1. Weigh 3 g. of potassium chloride, KCl.	1a. Use a trip balance. 1b. This is slightly more than is needed.	
	2. Dry it at 110°C.	2a. For 1 hour.	
	3. Cool it in a desiccator.	3a. For 30 minutes.	
	4. Weigh 1.907 g. of the potassium chloride, KCl.	4a. Use an analytical balance.	
	5. Transfer it to a 1 liter volumetric flask.	5a. Use deionized water in the plastic squeeze bottle.	

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
B. Reagent Preparation (continued)	6. Dissolve the salt in deionized water in the flask.		
	7. Dilute to the 1 liter mark.	7a. With deionized water.	
	8. Mix thoroughly.	8a. The concentration of this solution is 1.0 mg of potassium per 1.0 ml of solution.	
	9. If the expected potassium concentration in the sample is between 1.0 and 10.0 mg/liter, prepare the intermediate potassium solution (B.5 below).	9a. If there is doubt about the expected potassium concentration, both the intermediate and standard potassium solutions should be prepared, along with two calibration graphs.	
	10. If the expected potassium concentration is between 0.1 and 1.0 mg/liter, prepare the standard potassium solution (B.6 below).		
5. Intermediate Potassium Solution	1. Pipet 100.0 ml of the stock potassium solution (B.4.) into a 1 liter volumetric flask.		
	2. Dilute to the 1 liter mark.	2a. With deionized water.	
	3. Mix thoroughly.	3a. The concentration of this solution is 0.1 mg of potassium per 1.0 ml of solution.	

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
B. Reagent Preparation (continued)			
6. Standard Potassium Solution	1. Pipet 100.0 ml of the intermediate potassium solution (B.5.) into a 1 liter volumetric flask.		
	2. Dilute to the 1 liter mark.	2a. With deionized water.	
	3. Mix thoroughly.	3a. The concentration of this solution is 0.01 mg of potassium per 1.0 ml of solution.	
	4. Transfer the potassium solutions you have prepared to polyethylene bottles.		
C. Sample Collection	1. Collect the sample in a polyethylene bottle.	1a. Although only a few ml of sample are actually needed, a larger volume, such as 200 ml, is more convenient to work with.	
	2. Acidify the sample with distilled nitric acid, HNO_3.	2a. Use 5 ml of acid/liter of sample; 1.0 ml for 200 ml of sample. 2b. Measure the acid in a 10 ml graduated cylinder.	
	3. Gently swirl the bottle.	3a. To mix the acid and sample.	
	4. Check the pH of the sample.	4a. Use pH sensitive paper. 4b. It must be less than 2. If it is not, add a few more drops of acid, swirl the bottle, and recheck the pH. Repeat the procedure until the pH is less than 2. 4c. Do not store the sample for more than 6 months before completing the analysis.	

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
D. Sample Digestion	1. Shake the sample container.	1a. To ensure that it is homogeneous.	
	2. Measure 100 ml of the acidified sample.	2a. Use a 100 ml graduated cylinder.	
	3. Pour it into a 250 ml Erlenmeyer flask.	3a. If any solids remain in the cylinder, rinse them into the flask with a few ml of deionized water.	
	4. Measure 5 ml of 1 + 1 distilled hydrochloric acid, HCl.	4a. Use a 10 ml graduated cylinder.	
	5. Pour it into the flask.		
	6. Swirl the flask.	6a. To mix the acid and sample.	
	7. Put the flask on a hotplate.		
	8. Turn on the hotplate and adjust the temperature setting so the sample comes to a temperature of 95°C.	8a. Check the temperature of the sample with a thermometer. 8b. Do not allow the temperature of the sample to go above 95°C.	
	9. After the sample has come to 95°C, continue the heating for 15 min.	9a. During the 15 minute period, proceed with Step 10.	
	10. Assemble a filtration apparatus.	10a. A ring stand, a funnel (approximately 60 mm diameter), a ring to hold the funnel, and a piece of medium porosity filter paper (such as Whatman number 40). 10b. Use a clean 100 ml graduated cylinder as receiver.	

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
D. Sample Digestion (continued)	11. After the 15 min. heating period, remove the flask from the hotplate.	11a. Be cautious of the hot flask. Use a glove or tongs.	
	12. Allow it to cool at room temperature for about 15 min.		
	13. Filter the sample through the filter paper into the cylinder.	13a. Solids in the sample would clog the burner on the flame photometer.	
	14. Wash the filter paper with small portions (a few ml) of deionized water, and catch the washings in the cylinder.	14a. When the volume in the cylinder is 100 ml, remove the cylinder from under the funnel.	
	15. Cover the cylinder with an inverted 150 ml beaker.	15a. Until the analysis. 15b. To prevent contamination.	
E. Spectrophotometer Warm-up	1. Plug the power cord on the instrument into a wall outlet.	1a. 115 volts, 50/60 cycle.	
	2. Turn on the power toggle switch.	2a. The indicator light will go on. 2b. Do not turn on the lamp toggle switch. It is not used when making flame photometry measurements.	
	3. Allow the instrument to warm up for 45 minutes. While it is warming up, proceed with Section F.	3a. With older instruments, 2 hours or longer would be a better warm-up time.	

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
F. Preparation of Standards	1. While the instrument is warming up, prepare the potassium standards.	1a. Two standard potassium solutions were prepared. One concentration was 0.01 mg/ml (the standard potassium solution (B.6.), and the other was 0.1 mg/ml (the intermediate potassium solution (B.5.). Experience, or trial and error, will determine which potassium solution you use.	
	2. Assemble six 100 ml volumetric flasks.		
	3. Mark them 0, 2, 4, 6, 8, and 10 if you use the intermediate potassium solution (B.5., 0.1 mg/ml), or 0.0, 0.2, 0.4, 0.6, 0.8, and 1.0 if you use the standard potassium solution (B.6., 0.01 mg/ml).	3a. If you do not know which potassium solution to use, then prepare two sets of standards with six more 100 ml volumetric flasks and a second 10 ml graduated pipet. If you do know the expected potassium concentration in the sample, and therefore, which potassium solution to use, only one set of standards is needed.	
	4. Pipet 2.0 ml of the intermediate potassium solution into the flask marked 2, and 2.0 ml of the standard potassium solution into the flask marked 0.2.	4a. Use one 10 ml graduated pipet for the intermediate solution, and a second 10 ml graduated pipet for the standard solution.	
	5. Pipet 4.0 ml of the intermediate potassium solution into the flask marked 4, and 4.0 ml of the standard potassium solution into the flask marked 0.4.	5a. Use the appropriate pipet.	
	6. Prepare the 6, 8, and 10, and 0.6, 0.8, and 1.0 flasks in a similar manner.	6a. Use the appropriate pipet.	

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
F. Preparation of Standards (continued)	7. Add deionized water to the mark in each of the six or twelve flasks.		
	8. Mix thoroughly.	8a. The concentrations are: 0.0, 2.0, 4.0, 6.0, 8.0, and 10.0 mg/liter in the one set of standards, and 0.0, 0.2, 0.4, 0.6, 0.8, and 1.0 mg/liter in the other.	
G. Analysis			
1. Standards and Sample	1. Mark the 5 ml beakers (six or twelve) in the same way that the 100 ml volumetric flasks are marked.	1a. Either glass or plastic disposable. 1b. Used for aspirating solutions.	
	2. Pour the standards into the appropriate 5 ml beakers.	2a. Fill the beakers about three-fourths full. 2b. Caution: Throughout the remainder of this procedure, be careful not to get your fingers into any of the solutions. This could cause an error in the result.	
	3. Shake the sample thoroughly.	3a. Even if it was filtered earlier.	
	4. Fill another 5 ml beaker with sample.	4a. About three-fourths full.	
	5. Fill another 5 ml beaker with deionized water.	5a. About three-fourths full.	
2. Lighting the Flame	1. Raise the door on the right side of the burner housing.		

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
G. Analysis (continued)			
	2. Raise the sample positioner control between the instrument and the burner housing to the vertical position as far as it will go.	2a. Do not force the sample positioner control.	
	3. Close the oxygen and fuel (hydrogen) valves on top of the control panel.	3a. By turning them counter clockwise until they just begin to feel loose; i.e., until they can be wiggled very slightly left and right.	
	4. Close the low pressure valve on the regulators attached to the hydrogen and oxygen cylinders.	4a. By turning the handles counter-clockwise until they just begin to feel loose; i.e., until they can be wiggled very slightly left and right.	
	5. Close the fuel (hydrogen) needle valve on the right side of the control panel.	5a. By turning it clockwise with a screwdriver as far as it will go. 5b. Do not force the screwdriver.	
	6. Open the fuel (hydrogen) needle valve on the right side of the control panel.	6a. By turning it counter clockwise with a screwdriver. 6b. About 1/8 turn.	
	7. Open the main valve on the oxygen cylinder.	7a. By turning the handle counter clockwise two full turns. 7b. For safety, oxygen is always turned on first, and turned off last.	
	8. Open the low pressure valve on the oxygen cylinder.	8a. By turning the handle clockwise until the needle moves away from zero.	
	9. Set the pressure for 30 pounds per square inch.	9a. By turning the valve clockwise.	

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
6. Analysis (continued)	10. Open the oxygen valve on the control panel.	10a. By turning the handle clockwise until the needle moves away from zero.	
	11. Set the pressure for 13 pounds per square inch.	11a. By turning the handle clockwise. 11b. The actual oxygen pressure should be written on a tag attached to the atomizer burner. 11c. The optimum pressure may be checked if no tag is attached to the burner. 11d. Attach a small diameter piece of rubber or plastic tubing about 1 foot long to the brass tube extending from the bottom of the atomizer burner. The rubber or plastic tubing should fit the brass tube snugly. Place the other end of the rubber or plastic tubing in a 10 ml graduated cylinder. Fill it to the 10.0 line with deionized water. When the oxygen is flowing at the proper rate, the deionized water should be aspirated at the rate of 1.5 - 2.0 ml per minute. This rate corresponds to about thirteen pounds pressure per square inch.	
	12. Remove the tubing and cylinder.		
	13. Open the low pressure valve on the hydrogen cylinder.	13a. By turning the handle clockwise until the needle moves away from zero.	
	14. Set the pressure for 10 pounds per square inch.	14a. By turning the valve clockwise.	
	15. Open the fuel (hydrogen) valve on the control panel.	15a. By turning the handle clockwise.	
	16. Set the pressure for 4.5 pounds per square inch.		

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
G. Analysis (continued)	17. Cautiously bring a lighted match to the tip of the atomizer burner.	17a. The oxygen-hydrogen mixture will ignite with a loud pop and hissing sound.	
	18. Close the door on the right side of the burner housing.	18a. Caution: hot gases are escaping from the top of the coil. Do not place your hand or any other part of your body over the coil while the gases are burning.	
	19. Place the beaker containing the highest concentration standard (10 mg/liter or 1.0 mg/liter) into the holder.	19a. See figure 3. 19b. If two sets of standards are being used, take readings on the 10, 8, 6, 4, 2, and 0 mg/liter solutions first, and then the 1.0, 0.8, 0.6, 0.4, 0.2, and 0.0 mg/liter solutions. Do not mix the two sets of standards.	
	20. Swing the beaker into the burner housing compartment using the sample positioner control.	20a. A distinct change in sound will be heard as the solution is aspirated into the burner. 20b. For the remainder of this procedure, if the sound caused by the aspiration of a solution changes while the solution is being aspirated, it probably means that all of the liquid in the beaker has been aspirated, and the beaker is empty. 20c. Swing the beaker out of the burner housing, refill it with the appropriate solution, and swing it back into the burner housing. 20d. While the solution is aspirating, check that the hydrogen pressure is still 10 pounds per square inch and that the oxygen pressure is still at the optimum valve determined above. If one or both of the pressures have changed, reset them.	
	21. Turn the sensitivity knob to position 1.		
	22. Make the needle read 0% transmittance using the dark current knob.	22a. In this procedure, all readings will be made on the transmittance portion of the scale, not the absorbance portion.	

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
G. Analysis (continued)			
	23. Turn the sensitivity knob to position 4.		
	24. Repeat step 22.		
	25. Adjust the fuel needle valve so the tip of the flame comes to the top of the burner housing compartment, not to the top of the coil on top of the compartment.	25a. Use a screwdriver. 25b. Caution: extremely hot gases are escaping through the coil. 25c. Adjustment of this needle valve setting is not necessary each time the instrument is used, unless the setting has been changed for some reason.	
3. Aspiration of Standards and Sample	1. Turn the fltr-shtr-open knob to the open position.	1a. The shutter is open in this position. 1b. In the shtr position, the shutter is closed.	
	2. Turn the wavelength knob very slowly clockwise.	2a. Turn the knob continuously. Do not turn the knob in steps. 2b. One of three things will happen, 2c., 2d., or 2e. 2c. is the condition you are trying to achieve. 2c. First: the needle will move to the left, and at some % transmittance between 50 and 100, will suddenly swing back to the right. In this case, proceed to step 3. 2d. Second: the needle will swing back to the right as in 2c, but at some % transmittance between 0 and 50. In this case, proceed to step 4. 2e. Thirdly: the needle will swing back to the right, but at some point greater than 100% transmittance; or, it will not swing back to the right, it will stay to the left. In this case, proceed to step 9.	
	3. Record this wavelength and proceed to step 14.	3a. Use the example data sheet(s); see pages 29 & 30. 3b. Do not change this wavelength until the procedure instructs you to change it.	

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
G. Analysis (continued)		3c. This wavelength should be 768 nanometers. If it is too far away from this valve (less than 763, or more than 773), the calibration of the instrument should be checked using the instrument manual.	
	4. Close the shutter.		
	5. Increase the reading on the slit knob by 0.05 millimeter.	5a. It is graduated in tenths of a millimeter between 0.0 and 1.5 millimeters.	
	6. Turn the wavelength back to 760 nanometers.		
	7. Repeat steps 1 and 2.	7a. If condition 2d still exists, repeat steps 4 through 7 until the needle moves as described in 2c.	
	8. Record this wavelength and proceed to step 14.	8a. Use the example data sheet(s); see pages 29 & 30. 8b. Do not change this wavelength until the procedure instructs you to change it.	
	9. Close the shutter.		
	10. Decrease the reading on the slit knob by 0.05 millimeter.	10a. It is graduated in tenths of a millimeter between 0.0 and 1.5 millimeters.	
	11. Turn the wavelength back to 760 nanometers.		
	12. Repeat steps 1 and 2.	12a. If condition 2e still exists, repeat steps 9 through 11 until the needle moves as described in 2 c.	

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
G. Analysis (continued)			
	13. Record this wavelength and proceed to step 14.	13a. Use the example data sheet(s); see pages 29 & 30. 13b. Do not change this wavelength until the procedure instructs you to change it.	
	14. Turn the slit knob so as to make the needle read 100% transmittance.		
	15. Close the shutter.	15a. Do not change this setting until the procedure instructs you to change it.	
	16. Record a reading of 100% transmittance for the 10 or 1.0 mg/liter solution.	16a. Use the example data sheet(s); see pages 29 & 30. 16b. This first set of readings you will get on the one or two sets of standards and sample are called peak readings.	
	17. Swing the beaker out of the burner housing compartment.		
	18. Replace it with the 8 or 0.8 mg/liter solution.		
	19. Swing it into the burner housing compartment.		
	20. Open the shutter.		
	21. Record the % transmittance reading.	21a. Use the example data sheet(s); see pages 29 & 30.	
	22. Close the shutter.		

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
6. Analysis (continued)	23. Repeat steps 17 through 22 for the 6, 4, 2, and 0 mg/liter solutions and the sample, or the 0.6, 0.4, 0.2, and 0.0 mg/liter solutions and the sample.	23a. Use the example data sheet(s); see pages 29 & 30.	
	24. Swing the beaker of sample out of the burner housing compartment.		
	25. Replace it with the beaker of deionized water.		
	26. Swing it into the burner housing compartment.		
	27. Turn the dark current knob so the needle reads 0% transmittance.		
	28. Replace the beaker of deionized water with the beaker of the 10 or 1.0 mg/liter solution.	28a. It may need refilling.	
	29. Open the shutter.	29a. The needle should show 100% transmittance; it may be "off" by plus or minus 1 or 2% because of the dark current adjustment. Do not change the slit setting.	
	30. Turn the wavelength knob very slowly clockwise.	30a. Turn the knob continuously. Do not turn the knob, stop, and start again. 30b. The needle will move to the right. 30c. At some low % transmittance value, perhaps less than 1, or even 0, the needle will move no farther to the right.	

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
G. Analysis (continued)		30d. If there is some doubt as to when the needle stops moving to the right, turn the wavelength knob about one-quarter turn counter clockwise and repeat step 30.	
	31. Record this wavelength.	31a. Use the example data sheet(s); see pages 29 & 30. 31b. It is sometimes called the background wavelength. 31c. Do not change this wavelength setting for the remainder of the procedure.	
	32. Record this low % transmittance for the 10 or 1.0 mg/liter solution.	32a. Use the example data sheet(s); see pages 29 & 30. This second set of readings you will get on the one or two sets of standards and sample are called background readings.	
	33. Close the shutter.		
	34. Swing the beaker out of the burner housing compartment.		
	35. Replace it with the 8 or 0.8 mg/liter solution.		
	36. Swing it into the burner housing.		
	37. Open the shutter.		
	38. Record the % transmittance reading.	38a. Use the example data sheet(s); see pages 29 & 30.	
	39. Close the shutter.		
	40. Repeat steps 34 through 39 to obtain readings for the 6, 4, 2, and 0 mg/liter solutions and the sample, or the 0.6, 0.4, 0.2, and 0.0 mg/liter solutions, and the sample.		

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
G. Analysis (continued)	41. Replace the beaker of sample with the beaker of deionized water.		
	42. Allow the deionized water to aspirate for 10 seconds.		
	43. Swing the beaker of deionized water out of the burner housing.		
	44. Close the main valve on the hydrogen cylinder.	44a. By turning clockwise all the way.	
	45. When the hydrogen pressure registers 0 on the control panel hydrogen (fuel) gauge, close the main valve on the oxygen cylinder.	45a. By turning clockwise all the way.	
	46. Turn the sensitivity knob to the standby position.		
	47. Turn off the power toggle switch.		
	48. Empty all of the small beakers used.	48a. Don't forget the one still in the instrument. 48b. If the beakers are of the disposable type, discard them and proceed to H. If they are glass, do steps 49, 50, and 51.	
	49. Rinse the beakers thoroughly with tap water.		
	50. Rinse the beakers thoroughly with deionized water.		

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
G. Analysis (continued)	51. Allow the beakers to drain dry, and then proceed to Section H.		
H. Calculations	1. For all of the standards, subtract the % transmittance obtained at the background wavelength from the % transmittance obtained at the peak wavelength.	1a. Example: 10.0 mg/liter solution 100 = % transmittance at the peak wavelength 1 = % transmittance at the background wavelength 99 = % transmittance difference	
	2. On "regular" graph paper prepare a calibration graph using the % transmittance differences along the vertical axis, and the corresponding concentrations (10, 8, 6, 4, 2, 0, or 1.0, 0.8, 0.6, 0.4, 0.2, 0.0 mg/liter) on the horizontal axis.	2a. If you have used both sets of standards (the intermediate and standard potassium solutions), prepare two calibration graphs. Pages 31 and 32 are sheets of "regular" graph paper. 2b. "Regular" graph paper is marked off in squares of equal size. 2c. EMP CH.IN.cg.EMP.1a.1.77 may be referred to for specific instructions in calibration graph preparation and use. 2d. In the case of the intermediate potassium solution, the calibration graph may have a slight bend.	
	3. Repeat step 1 for the sample.		
	4. Determine the potassium concentration in the sample.	4a. Using the calibration graph.	
	5. Record the result in mg/liter.	5a. Use the example data sheet(s); see pages 29 & 30.	

EXAMPLE
DATA SHEET

	Concentration of Potassium Standards in mg/liter	% Transmittance at the Peak Wavelength; Peak Readings	% Transmittance at the Background Wavelength; Background Readings	% Transmittance Differences; Values in 2nd Column Minus Values in 3rd Col.
	______*	______	______	______
	______	______	______	______
	______	______	______	______
	______	______	______	______
	______	______	______	______
	______	______	______	______
Sample		______	______	______

Concentration of potassium in the sample in mg/liter ______

Peak Wavelength ________ nm

Background Wavelength ________ nm

---

* The six values in this column will be 0, 2, 4, 6, 8, and 10, or, 0.0, 0.2, 0.4, 0.6, 0.8, and 1.0. If both sets of standards were used, use a second data sheet exactly like this one; see page 30.

EXAMPLE
DATA SHEET
(See the paragraph at the bottom of Page 29)

Concentration of Potassium Standards in mg/liter	%Transmittance at the Peak Wavelength; Peak Readings	%Transmittance at the Background Wavelength; Background Readings	%Transmittance Differences; Values in 2nd Column Minus Values in 3rd Col.
____	____	____	____
____	____	____	____
____	____	____	____
____	____	____	____
____	____	____	____
____	____	____	____
Sample	____	____	____

Concentration of potassium in the sample in mg/liter ____

Peak Wavelength ______nm
Background Wavelength ______nm

TRAINING GUIDE

SECTION	TOPIC
I	Introduction
II	Educational Concepts - Mathematics
III	Educational Concepts - Science
IV	Educational Concepts - Communications
V*	Field and Laboratory Equipment
VI	Field and Laboratory Reagents
VII	Field and Laboratory Analysis
VIII	Safety
IX	Records & Reports

* Training guide materials are presented here under the headings marked *.

A.1.1

If the glassware is especially dirty and cannot be cleaned with ordinary detergents, chromic acid cleaning may be required.

1. Pour 35 ml of distilled water in a 250 ml beaker.

Standard Methods, 14th ed., P. 336, section 2c.2)

2. Add about 1/8 teaspoon (simply estimate this quantity) of sodium dichromate, $Na_2Cr_2O_7$, to the water.
3. Swirl the beaker until the sodium dichromate has dissolved.
4. Keep repeating steps 2 and 3 until no more sodium dichromate will dissolve.
5. Pour the solution into a 2 liter beaker.
6. Slowly pour 1 liter of concentrated sulfuric acid, H_2SO_4, into the 2 liter beaker.

   Caution: Use eyeglasses and protective clothing.
7. Stir the mixture thoroughly.
8. Store it in a glass stoppered bottle.
9. The cleaning solution should be at a temperature of about 50°C when it is used.
10. It may therefore be necessary to warm the cleaning solution.
11. When using the warm cleaning solution, fill the piece of glassware with the solution.
12. Allow it to soak for 2-3 minutes (or longer).
13. Pour the cleaning solution back into the storage bottle.
14. Rinse the piece of glassware ten times with tap water.
15. The cleaning solution may be reused until it turns green.
16. It should then be discarded.

A PROTOTYPE FOR DEVELOPMENT OF ROUTINE OPERATIONAL PROCEDURES

for the

DETERMINATION OF SODIUM USING FLAME PHOTOMETRY

as applied in

WASTEWATER TREATMENT FACILITIES
and in the
MONITORING OF EFFLUENT WASTEWATERS

Developed by the

National Training and Operational Technology Center
Municipal Operations and Training Division
Office of Water Program Operations
U.S. Environmental Protection Agency

EFFLUENT MONITORING PROCEDURE: Determination of Sodium Using Flame Photometry

This operational procedure was developed by:

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ADDRESS EPA, OWPO, NTOTC, Cincinnati, Ohio 45268

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EDUCATION AND TECHNICAL BACKGROUND

B.S. - Chemistry

M.S. - Chemistry

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4 years additional Graduate School

4 years college Chemistry Instructor

1-1/2 years DHEW - Air Pollution Program, Chemist

10 years DI - EPA, Chemist-Instructor

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EFFLUENT MONITORING PROCEDURE: Determination of Sodium Using Flame Photometry

1. Analysis Objective:

The learner will determine the sodium content of a sewage effluent.

2. Brief Description of Analysis:

The learner will prepare a calibration graph using the percent transmittance and the concentration of a series of standard sodium solutions. The percent transmittance of a sample of sewage effluent will next be determined, and the sodium concentration found by using the calibration graph.

The work will be done using a Beckman Model B spectrophotometer with flame photometry attachments. Although this procedure has been prepared for use with a specific instrument, other equivalent commercially available instruments may of course be used. Mention of a particular brand name does not constitute endorsement by the U.S. Environmental Protection Agency.

3. Applicability of this Procedure:

a. Range of Concentration:

Concentration levels as low as 0.1 mg/liter can be detected in a good flame photometer. Although the cited reference (below) does not specifically state the highest sodium concentration which may be determined, a limit of 10 mg/liter may be inferred. Therefore, sample dilution may be required.

b. Pretreatment of Samples:

The digestion procedure referenced in the Federal Register, Wednesday, December 1, 1976, Part II, table I, footnote 15 (Methods for Chemical Analysis of Water & Wastes, 1974, page 83, par. 4.1.4.) is given in this effluent monitoring procedure.

c. Treatment of Interferences in the Sample:

When the following ratios are exceeded, an interference in the determination of sodium is present, and the cited reference must be consulted.

Ratio	Value of the Ratio
potassium/sodium	5/1
calcium/sodium	10/1
magnesium/sodium	100/1

Chloride, sulfate, and bicarbonate in relatively large amounts can cause radiation interference.

This procedure was taken from the Standard Methods, 14th ed., pg. 250, Method 320 A, and from the Beckman Instrument Manual.

EFFLUENT MONITORING PROCEDURE: Determination of Sodium Using Flame Photometry

Equipment and Supply Requirements

A. Capital Equipment:

1. Beckman Model B. spectrophotometer with flame photometer attachments and instrument manual
2. Source of distilled water
3. Source of deionized water
4. Oven, for use at 140°C.
5. Analytical balance, 100 g capacity

B. Reusable Supplies:

1. Trip balance, 100 g capacity
2. Pencil or pen
3. Twelve inch ruler
4. Graduated cylinder, 50 ml (for glassware cleaning)
5. Beaker, 150 ml
6. Beaker, 250 ml (for glassware cleaning)
7. Beaker, 2 liter (for glassware cleaning)
8. Laboratory apron
9. Safety glasses
10. Glass stoppered bottle, 1 liter (for storage of cleaning solution)
11. Three polyethylene bottles, 200 ml
12. One or two polyethylene bottles, 1 liter. (See page 7-13, steps 9 and 10.)
13. Graduated cylinder, 250 ml
14. Erlenmeyer flask, 125 ml
15. Erlenmeyer flask, 500 ml
16. Graduated cylinder, 100 ml
17. Graduated cylinder, 10 ml
18. Plastic weighing boat, about 2 inches square
19. Small spatula
20. One or two volumetric flasks, 1 liter (See page 7-13, 9a.)
21. Pipet, 100 ml
22. Two plastic squeeze bottles
23. Funnel, about 60 mm diameter
24. One piece Whatman number 40 (or equivalent) filter paper (to fit the funnel)
25. One ring (to support the funnel)
26. Six, or twelve, volumetric flasks, 100 ml (see page 7-17, 3a.)
27. One pipet bulb
28. One or two graduated pipets, 10 ml (See page 7-17, 3a.)
29. Eight, or sixteen, small beakers (depending on whether one or both sets of standards are prepared); either glass (supplied with the flame photometer) or disposable plastic, and used to hold solutions for aspiration
30. Two pressure regulators (one for hydrogen, one for oxygen)
31. Wrenches for use in attaching pressure regulators to gas cylinders
32. Wrench for use in making hose connections
33. Two clamps (for safely anchoring gas cylinders)
34. Screwdriver, medium size
35. One ring stand
36. Hot plate

B. Reusable Supplies (Continued)

37. Thermometer, 100°C
38. One piece of rubber or plastic tubing to fit onto the tube extending from the bottom of the atomizer burner, 1 ft.
39. Asbestos gloves or crucible tongs
40. One piece of pH sensitive paper (to measure a pH of 2)

C. Consumable Supplies:

1. Sodium chloride, NaCl, 3 g.
2. One piece graph paper; divided into squares of equal size
3. Sodium dichromate, $Na_2Cr_2O_7$ (for cleaning glassware)
4. Concentrated sulfuric acid, H_2SO_4 (for cleaning glassware)
5. Soap (for cleaning glassware)
6. Brush (for cleaning glassware)
7. Brush (for cleaning balance)
8. Paper towels
9. Matches
10. Concentrated nitric acid, HNO_3
11. Cylinder of hydrogen gas (for use with the flame photometer)
12. Cylinder of oxygen gas (for use with the flame photometer)
13. Concentrated hydrochloric acid, HCl
14. Distilled concentrated nitric acid, HNO_3*

All reagents should be of high quality. Different chemical manufacturers may have different ways of indicating a high quality reagent. While no endorsement of one chemical manufacturer over another is intended, the following are some designations used in four chemical catalogs to indicate high quality reagents.

Catalog	Designations
Thomas	Reagent, ACS, Chemically (Pure (CP)
Matheson, Coleman & Bell	Reagent, ACS
Curtin Matheson Scientific, Inc.	Primary Standard, ACS, AR
Fisher	Certified, ACS

* This reagent is used for acidifying the sample at the time of collection. It must be of higher purity than Reagent, ACS, etc. J. T. Baker "Ultrex" nitric acid is an example of a higher purity acid.

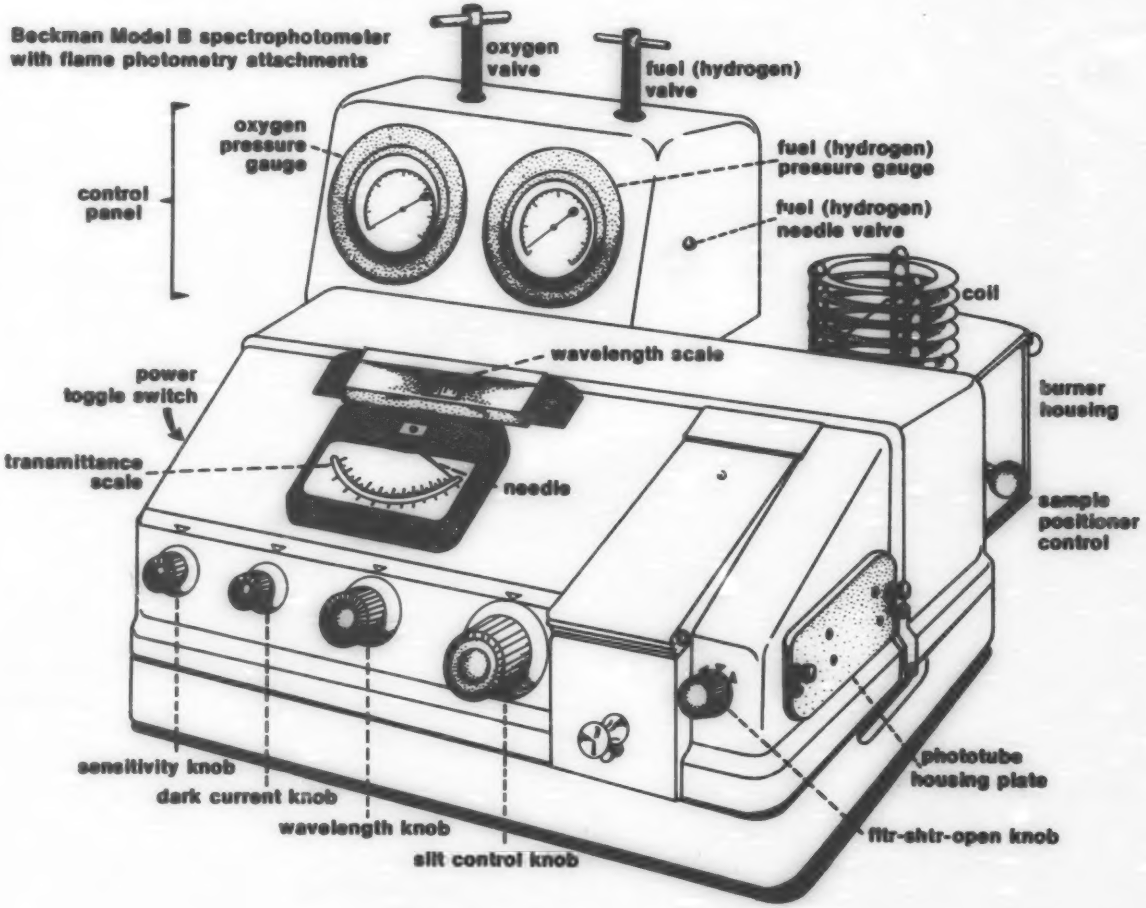
Beckman Model B spectrophotometer
with flame photometry attachments
oxygen valve
fuel (hydrogen) valve
oxygen pressure gauge
control panel
fuel (hydrogen) pressure gauge
fuel (hydrogen) needle valve
coil
wavelength scale
power toggle switch
burner housing
transmittance scale
needle
sample positioner control
sensitivity knob
dark current knob
wavelength knob
slit control knob
phototube housing plate
fltr-shtr-open knob

Figure 1

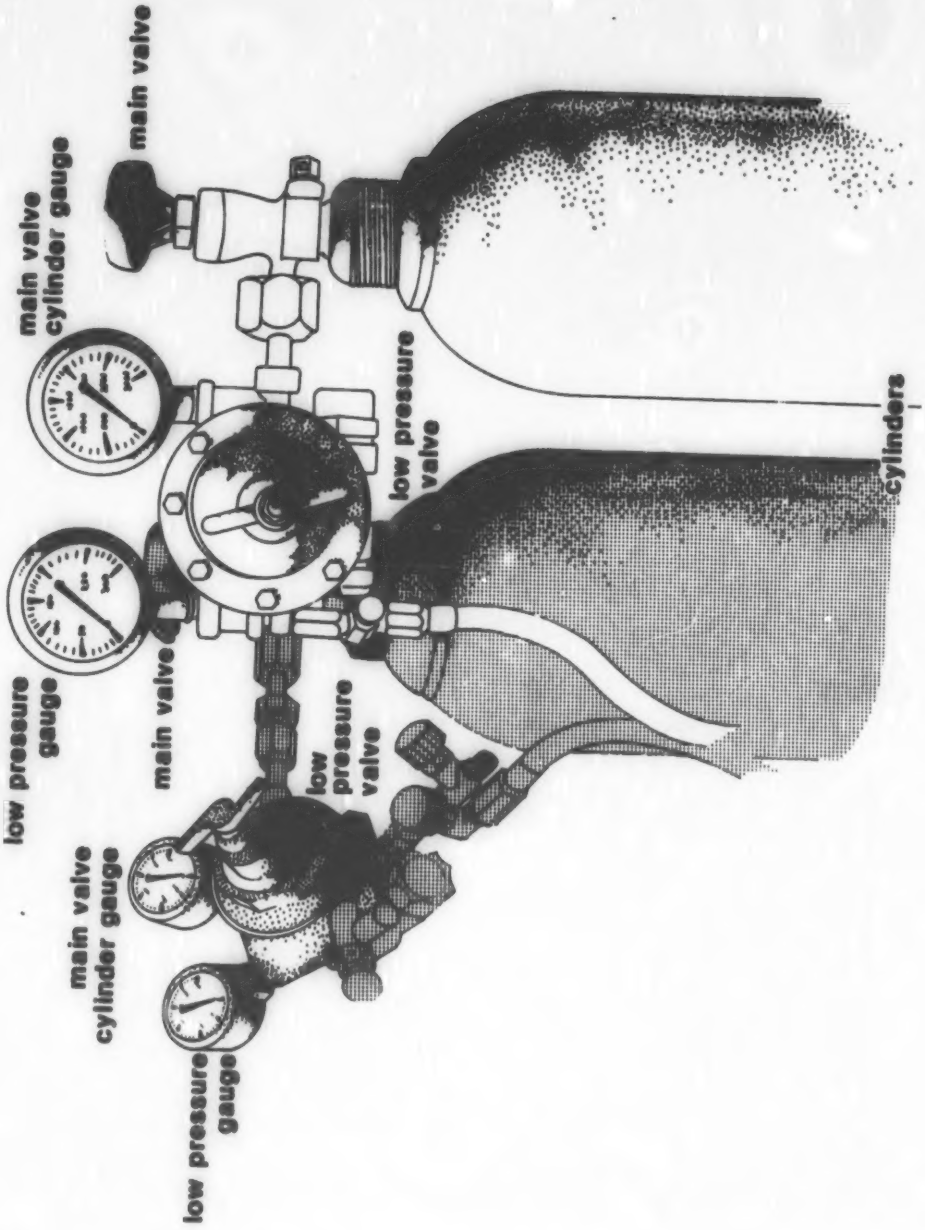
main valve
main valve cylinder gauge
low pressure valve
cylinders
low pressure gauge
main valve
low pressure valve
main valve cylinder gauge
low pressure gauge

Figure 2

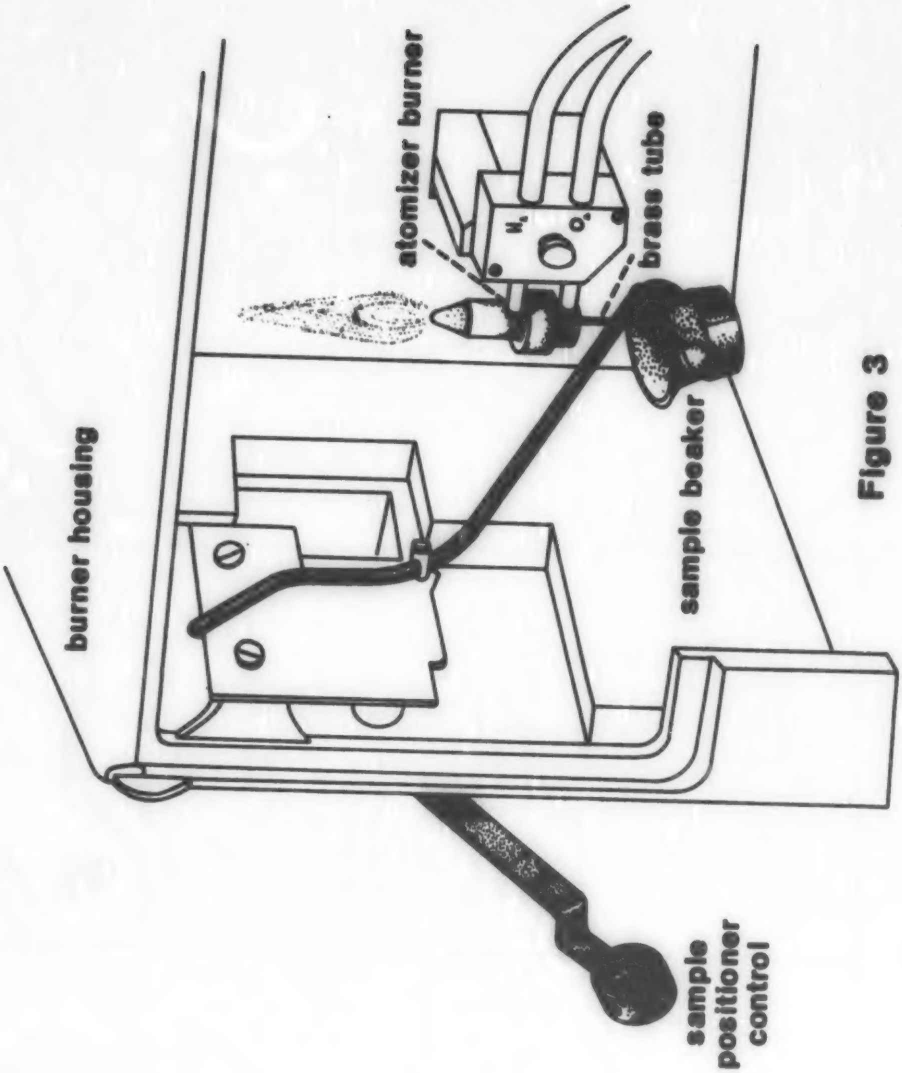
burner housing
atomizer burner
H_2
O_2
brass tube
sample beaker
sample positioner control

Figure 3

EFFLUENT MONITORING PROCEDURE: Determination of Sodium Using Flame Photometry

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
A. Equipment Preparation			V.A.1.1
1. Cleaning of Glassware	1. Clean all glassware and polyethylene bottles.		
	2. Rinse with nitric acid solution.	2a. Preparation of the acid is described in B.1.	
	3. Rinse with tap water	3a. Ten times.	
	4. Rinse with deionized water.	4a. Five times.	
2. Balance Preparation	1. Check the analytical balance for cleanliness and proper operation.	1a. Consult the manufacturer's manual if the balance does not operate properly.	
3. Spectrophotometer	1. Attach the oxygen and hydrogen cylinders to the Beckman Model B spectrophotometer with flame photometry attachments.	1a. Consult the manufacturer's manual for specific instructions. 1b. For the remainder of this procedure, the words instrument, or flame photometer, will be used to mean this particular instrument.	
	2. Turn the wavelength knob to a reading of 580 nanometers.		
	3. Turn the slit control knob to a reading of 0.4 mm.		
	4. Turn the sensitivity knob to the standby position.		
	5. Turn the fltr-shtr-open knob to the shtr position.	5a. This is the closed position.	

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
A. Equipment Preparation (Continued)			
4. Phototube	1. Remove the phototube housing plate (see Figure 1).	1a. The blue sensitive phototube should be used for sodium determination. 1b. Refer to figures 1, 2, & 3 when other parts of the instrument are mentioned in this procedure.	
	2. Check the condition of the desiccant in the phototube compartment.	2a. It may need drying at 103-105°C for 1 hour, followed by cooling in a desiccator for 30 min. 2b. The spectrophotometer will be turned on in E.	
B. Reagent Preparation			
1. Nitric Acid, HNO$_3$, Solution, 1 + 15	1. Measure 150 ml of distilled water.	1a. Use a 250 ml graduated cylinder.	
	2. Pour it into a 500 ml Erlenmeyer flask.		
	3. Measure 10 ml of concentrated nitric acid, HNO$_3$.	3a. Use a 10 ml graduated cylinder.	
	4. Pour the nitric acid slowly into the distilled water.		
	5. Swirl the flask.	5a. To mix the acid and water.	
	6. Store the solution in a polyethylene bottle.	6a. This solution is used for rinsing glassware and polyethylene bottles. 6b. Larger amounts may be prepared using the same proportion of acid and water.	

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
B. Reagent Preparation (continued)			
2. Nitric Acid, HNO_3, Distilled	1. See 1a.	1a. This reagent is used undiluted for acidifying the sample at the time of collection.	
3. Hydrochloric Acid, HCl, Distilled, 1 + 1	1. Measure 2.5 ml of distilled hydrochloric acid, HCl.	1a. Use a 10 ml graduated cylinder. 1b. Five ml of the 1 + 1 mixture are needed for each sample. Therefore, larger volumes may be prepared as necessary.	
	2. Pour it into a 125 ml Erlenmeyer flask.	2a. Use a larger flask if larger amounts of the mixture are being prepared.	
	3. Measure 2.5 ml of deionized water.	3a. Use the 10 ml graduated cylinder from 1a.	
	4. Pour it into the same flask.		
	5. Swirl the flask.	5a. To mix the acid and water.	
	6. Store the solution in a polyethylene bottle.		
4. Stock Sodium Solution	1. Weigh 3 g. of sodium chloride, NaCl.	1a. Use a trip balance. 1b. This is slightly more than is needed.	
	2. Dry it at 140°C.	2a. For 1 hour.	
	3. Cool it in a desiccator.	3a. For 30 minutes.	
	4. Weigh 2.542 g. of the sodium chloride, NaCl.	4a. Use an analytical balance.	
	5. Transfer it to a 1 liter volumetric flask.	5a. Use deionized water in the plastic squeeze bottle.	

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
B. Reagent Preparation (continued)	6. Dissolve the salt in deionized water in the flask.		
	7. Dilute to the 1 liter mark.	7a. With deionized water.	
	8. Mix thoroughly.	8a. The concentration of this solution is 1.0 mg of sodium per 1.0 ml of solution.	
	9. If the expected sodium concentration in the sample is between 1.0 and 10.0 mg/liter, prepare the intermediate sodium solution (B.5 below).	9a. If there is doubt about the expected sodium concentration, both the intermediate and standard sodium solutions should be prepared, along with two calibration graphs.	
	10. If the expected sodium concentration is between 0.1 and 1.0 mg/liter, prepare the standard sodium solution (B.6 below).		
5. Intermediate Sodium Solution	1. Pipet 100.0 ml of the stock sodium solution (B.4.) into a 1 liter volumetric flask.		
	2. Dilute to the 1 liter mark.	2a. With deionized water.	
	3. Mix thoroughly.	3a. The concentration of this solution is 0.1 mg of sodium per 1.0 ml of solution.	

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
B. Reagent Preparation (continued)			
6. Standard Sodium Solution	1. Pipet 100.0 ml of the intermediate sodium solution (B.5.) into a 1 liter volumetric flask.		
	2. Dilute to the 1 liter mark.	2a. With deionized water.	
	3. Mix thoroughly.	3a. The concentration of this solution is 0.01 mg of sodium per 1.0 ml of solution.	
	4. Transfer the sodium solutions you have prepared to polyethylene bottles.		
C. Sample Collection	1. Collect the sample in a polyethylene bottle.	1a. Although only a few ml of sample are actually needed, a larger volume, such as 200 ml, is more convenient to work with.	
	2. Acidify the sample with distilled nitric acid. HNO_3.	2a. Use 5 ml of acid/liter of sample; 1.0 ml for 200 ml of sample. 2b. Measure the acid in a 10 ml graduated cylinder.	
	3. Gently swirl the bottle.	3a. To mix the acid and sample.	
	4. Check the pH of the sample.	4a. Use pH sensitive paper. 4b. It must be less than 2. If it is not, add a few more drops of acid, swirl the bottle, and recheck the pH. Repeat the procedure until the pH is less than 2. 4c. Do not store the sample for more than 6 months before completing the analysis.	

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
D. Sample Digestion	1. Shake the sample container.	1a. To ensure that it is homogeneous.	
	2. Measure 100 ml of the acidified sample.	2a. Use a 100 ml graduated cylinder.	
	3. Pour it into a 250 ml Erlenmeyer flask.	3a. If any solids remain in the cylinder, rinse them into the flask with a few ml of deionized water.	
	4. Measure 5 ml of 1 + 1 distilled hydrochloric acid, HCl.	4a. Use a 10 ml graduated cylinder.	
	5. Pour it into the flask.		
	6. Swirl the flask.	6a. To mix the acid and sample.	
	7. Put the flask on a hotplate.		
	8. Turn on the hotplate and adjust the temperature setting so the sample comes to a temperature of 95°C.	8a. Check the temperature of the sample with a thermometer. 8b. Do not allow the temperature of the sample to go above 95°C.	
	9. After the sample has come to 95°C, continue the heating for 15 min.	9a. During the 15 minute period, proceed with Step 10.	
	10. Assemble a filtration apparatus.	10a. A ring stand, a funnel (approximately 60 mm diameter), a ring to hold the funnel, and a piece of medium porosity filter paper (such as Whatman number 40). 10b. Use a clean 100 ml graduated cylinder as receiver.	

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
D. Sample Digestion (continued)	11. After the 15 min. heating period, remove the flask from the hotplate.	11a. Be cautious of the hot flask. Use a glove or tongs.	
	12. Allow it to cool at room temperature for about 15 min.		
	13. Filter the sample through the filter paper into the cylinder.	13a. Solids in the sample would clog the burner on the flame photometer.	
	14. Wash the filter paper with small portions (a few ml) of deionized water, and catch the washings in the cylinder.	14a. When the volume in the cylinder is 100 ml, remove the cylinder from under the funnel.	
	15. Cover the cylinder with an inverted 150 ml beaker.	15a. Until the analysis. 15b. To prevent contamination.	
E. Spectrophotometer Warm-up	1. Plug the power cord on the instrument into a wall outlet.	1a. 115 volts, 50/60 cycle.	
	2. Turn on the power toggle switch.	2a. The indicator light will go on. 2b. Do not turn on the lamp toggle switch. It is not used when making flame photometry measurements.	
	3. Allow the instrument to warm up for 45 minutes. While it is warming up, proceed with Section F.	3a. With older instruments, 2 hours or longer would be a better warm-up time.	

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
F. Preparation of Standards.	1. While the instrument is warming up, prepare the sodium standards.	1a. Two standard sodium solutions were prepared. One concentration was 0.01 mg/ml (the standard sodium solution (B.6.), and the other was 0.1 mg/ml (the intermediate sodium solution (B.5.). Experience, or trial and error, will determine which sodium solution you use.	
	2. Assemble six 100 ml volumetric flasks.		
	3. Mark them 0, 2, 4, 6, 8, and 10 if you use the intermediate sodium solution (B.5., 0.1 mg/ml), or 0.0, 0.2, 0.4, 0.6, 0.8, and 1.0 if you use the standard sodium solution (B.6., 0.01 mg/ml).	3a. If you do not know which sodium solution to use, then prepare two sets of standards with six more 100 ml volumetric flasks and a second 10 ml graduated pipet. If you do know the expected sodium concentration in the sample, and therefore, which sodium solution to use, only one set of standards is needed.	
	4. Pipet 2.0 ml of the intermediate sodium solution into the flask marked 2, and 2.0 ml of the standard sodium solution into the flask marked 0.2.	4a. Use one 10 ml graduated pipet for the intermediate solution, and a second 10 ml graduated pipet for the standard solution.	
	5. Pipet 4.0 ml of the intermediate sodium solution into the flask marked 4, and 4.0 ml of the standard sodium solution into the flask marked 0.4.	5a. Use the appropriate pipet.	
	6. Prepare the 6, 8, and 10, and 0.6, 0.8, and 1.0 flasks in a similar manner.	6a. Use the appropriate pipet.	

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
F. Preparation of Standards (continued)	7. Add deionized water to the mark in each of the six or twelve flasks.		
	8. Mix thoroughly.	8a. The concentrations are: 0.0, 2.0, 4.0, 6.0, 8.0, and 10.0 mg/liter in the one set of standards, and: 0.0, 0.2, 0.4, 0.6, 0.8, and 1.0 mg/liter in the other.	
G. Analysis			
1. Standards and Sample	1. Mark the 5 ml beakers (six or twelve) in the same way that the 100 ml volumetric flasks are marked.	1a. Either glass or plastic disposable. 1b. Used for aspirating solutions.	
	2. Pour the standards into the appropriate 5 ml beakers.	2a. Fill the beakers about three-fourths full. 2b. Caution: Throughout the remainder of this procedure, be careful not to get your fingers into any of the solutions. This could cause an error in the result.	
	3. Shake the sample thoroughly.	3a. Even if it was filtered earlier.	
	4. Fill another 5 ml beaker with sample.	4a. About three-fourths full.	
	5. Fill another 5 ml beaker with deionized water.	5a. About three-fourths full.	
2. Lighting the Flame	1. Raise the door on the right side of the burner housing.		

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
G. Analysis (continued)	2. Raise the sample positioner control between the instrument and the burner housing to the vertical position as far as it will go.	2a. Do not force the sample positioner control.	
	3. Close the oxygen and fuel (hydrogen) valves on top of the control panel.	3a. By turning them counter clockwise until they just begin to feel loose; i.e., until they can be wiggled very slightly left and right.	
	4. Close the low pressure valve on the regulators attached to the hydrogen and oxygen cylinders.	4a. By turning the handles counter clockwise until they just begin to feel loose; i.e., until they can be wiggled very slightly left and right.	
	5. Close the fuel (hydrogen) needle valve on the right side of the control panel.	5a. By turning it clockwise with a screwdriver as far as it will go. 5b. Do not force the screwdriver.	
	6. Open the fuel (hydrogen) needle valve on the right side of the control panel.	6a. By turning it counter clockwise with a screwdriver. 6b. About 1/8 turn.	
	7. Open the main valve on the oxygen cylinder.	7a. By turning the handle counter clockwise two full turns. 7b. For safety, oxygen is always turned on first, and turned off last.	
	8. Open the low pressure valve on the oxygen cylinder.	8a. By turning the handle clockwise until the needle moves away from zero.	
	9. Set the pressure for 30 pounds per square inch.	9a. By turning the valve clockwise.	

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
G. Analysis (continued)	10. Open the oxygen valve on the control panel.	10a. By turning the handle clockwise until the needle moves away from zero.	
	11. Set the pressure for 13 pounds per square inch.	11a. By turning the handle clockwise. 11b. The actual oxygen pressure should be written on a tag attached to the atomizer burner. 11c. The optimum pressure may be checked if no tag is attached to the burner. 11d. Attach a small diameter piece of rubber or plastic tubing about 1 foot long to the brass tube extending from the bottom of the atomizer burner. The rubber or plastic tubing should fit the brass tube snugly. Place the other end of the rubber or plastic tubing in a 10 ml graduated cylinder. Fill it to the 10.0 line with deionized water. When the oxygen is flowing at the proper rate, the deionized water should be aspirated at the rate of 1.5 - 2.0 ml per minute. This rate corresponds to about thirteen pounds pressure per square inch.	
	12. Remove the tubing and cylinder.		
	13. Open the low pressure valve on the hydrogen cylinder.	13a. By turning the handle clockwise until the needle moves away from zero.	
	14. Set the pressure for 10 pounds per square inch.	14a. By turning the valve clockwise.	
	15. Open the fuel (hydrogen) valve on the control panel.	15a. By turning the handle clockwise.	
	16. Set the pressure for 4.5 pounds per square inch.		

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
6. Analysis (continued)			
	17. Cautiously bring a lighted match to the tip of the atomizer burner.	17a. The oxygen-hydrogen mixture will ignite with a loud pop and hissing sound.	
	18. Close the door on the right side of the burner housing.	18a. Caution: hot gases are escaping from the top of the coil. Do not place your hand or any other part of your body over the coil while the gases are burning.	
	19. Place the beaker containing the highest concentration standard (10 mg/liter or 1.0 mg/liter) into the holder.	19a. See figure 3. 19b. If two sets of standards are being used, take readings on the 10, 8, 6, 4, 2, and 0 mg/liter solutions first, and then the 1.0, 0.8, 0.6, 0.4, 0.2, and 0.0 mg/liter solutions. Do not mix the two sets of standards.	
	20. Swing the beaker into the burner housing compartment using the sample positioner control.	20a. A distinct change in sound will be heard as the solution is aspirated into the burner. 20b. For the remainder of this procedure, if the sound caused by the aspiration of a solution changes while the solution is being aspirated, it probably means that all of the liquid in the beaker has been aspirated, and the beaker is empty. 20c. Swing the beaker out of the burner housing, refill it with the appropriate solution, and swing it back into the burner housing. 20d. While the solution is aspirating, check that the hydrogen pressure is still 10 pounds per square inch and that the oxygen pressure is still at the optimum valve determined above. If one or both of the pressures have changed, reset them.	
	21. Turn the sensitivity knob to position 1.		
	22. Make the needle read 0% transmittance using the dark current knob.	22a. In this procedure, all readings will be made on the transmittance portion of the scale, not the absorbance portion.	

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
G. Analysis (continued)			
	23. Turn the sensitivity knob to position 4.		
	24. Repeat step 22.		
	25. Adjust the fuel needle valve so the tip of the flame comes to the top of the burner housing compartment, not to the top of the coil on top of the compartment.	25a. Use a screwdriver. 25b. Caution: extremely hot gases are escaping through the coil. 25c. Adjustment of this needle valve setting is not necessary each time the instrument is used, unless the setting has been changed for some reason.	
3. Aspiration of Standards and Sample	1. Turn the fltr-shtr-open knob to the open position.	1a. The shutter is open in this position. 1b. In the shtr position, the shutter is closed.	
	2. Turn the wavelength knob very slowly clockwise.	2a. Turn the knob continuously. Do not turn the knob in steps. 2b. One of three things will happen, 2c., 2d., or 2e. 2c. is the condition you are trying to achieve. 2c. First: the needle will move to the left, and at some % transmittance between 50 and 100, will suddenly swing back to the right. In this case, proceed to step 3. 2d. Second: the needle will swing back to the right as in 2c, but at some % transmittance between 0 and 50. In this case, proceed to step 4. 2e. Thirdly: the needle will swing back to the right, but at some point greater than 100% transmittance; or, it will not swing back to the right, it will stay to the left. In this case, proceed to step 9.	
	3. Record this wavelength and proceed to step 14.	3a. Use the example data sheet(s); see pages 29 & 30. 3b. Do not change this wavelength until the procedure instructs you to change it.	

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
G. Analysis (continued)		3c. This wavelength should be 589 nanometers. If it is too far away from this valve (less than 584, or more than 594), the calibration of the instrument should be checked using the instrument manual.	
	4. Close the shutter.		
	5. Increase the reading on the slit knob by 0.05 millimeter.	5a. It is graduated in tenths of a millimeter between 0.0 and 1.5 millimeters.	
	6. Turn the wavelength back to 580 nanometers.		
	7. Repeat steps 1 and 2.	7a. If condition 2d still exists, repeat steps 4 through 7 until the needle moves as described in 2c.	
	8. Record this wavelength and proceed to step 14.	8a. Use the example data sheet(s); see pages 29 & 30. 8b. Do not change this wavelength until the procedure instructs you to change it.	
	9. Close the shutter.		
	10. Decrease the reading on the slit knob by 0.05 millimeter.	10a. It is graduated in tenths of a millimeter between 0.0 and 1.5 millimeters.	
	11. Turn the wavelength back to 580 nanometers.		
	12. Repeat steps 1 and 2.	12a. If condition 2e still exists, repeat steps 9 through 11 until the needle moves as described in 2c.	

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
6. Analysis (continued)			
	13. Record this wavelength and proceed to step 14.	13a. Use the example data sheet(s); see pages 29 & 30. 13b. Do not change this wavelength until the procedure instructs you to change it.	
	14. Turn the slit knob so as to make the needle read 100% transmittance.		
	15. Close the shutter.	15a. Do not change this setting until the procedure instructs you to change it.	
	16. Record a reading of 100% transmittance for the 10 or 1.0 mg/liter solution.	16a. Use the example data sheet(s); see pages 29 & 30. 16b. This first set of readings you will get on the one or two sets of standards and sample are called peak readings.	
	17. Swing the beaker out of the burner housing compartment.		
	18. Replace it with the 8 or 0.8 mg/liter solution.		
	19. Swing it into the burner housing compartment.		
	20. Open the shutter.		
	21. Record the % transmittance reading.	21a. Use the example data sheet(s); see pages 29 & 30.	
	22. Close the shutter.		

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
6. Analysis (continued)	23. Repeat steps 17 through 22 for the 6, 4, 2, and 0 mg/liter solutions and the sample, or the 0.6, 0.4, 0.2, and 0.0 mg/liter solutions and the sample.	23a. Use the example data sheet(s); see pages 29 & 30.	
	24. Swing the beaker of sample out of the burner housing compartment.		
	25. Replace it with the beaker of deionized water.		
	26. Swing it into the burner housing compartment.		
	27. Turn the dark current knob so the needle reads 0% transmittance.		
	28. Replace the beaker of deionized water with the beaker of the 10 or 1.0 mg/liter solution.	28a. It may need refilling.	
	29. Open the shutter.	29a. The needle should show 100% transmittance; it may be "off" by plus or minus 1 or 2% because of the dark current adjustment. Do not change the slit setting.	
	30. Turn the wavelength knob very slowly clockwise.	30a. Turn the knob continuously. Do not turn the knob, stop, and start again. 30b. The needle will move to the right. 30c. At some low % transmittance value, perhaps less than 1, or even 0, the needle will move no farther to the right.	

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
G. Analysis (continued)		30d. If there is some doubt as to when the needle stops moving to the right, turn the wavelength knob about one-quarter turn, counter clockwise and repeat step 30.	
	31. Record this wavelength.	31a. Use the example data sheet(s); see pages 29 & 30. 31b. It is sometimes called the background wavelength. 31c. Do not change this wavelength setting for the remainder of the procedure.	
	32. Record this low % transmittance for the 10 or 1.0 mg/liter solution.	32a. Use the example data sheet(s); see pages 29 & 30. This second set of readings you will get on the one or two sets of standards and sample are called background readings.	
	33. Close the shutter.		
	34. Swing the beaker out of the burner housing compartment.		
	35. Replace it with the 8 or 0.8 mg/liter solution.		
	36. Swing it into the burner housing.		
	37. Open the shutter.		
	38. Record the % transmittance reading.	38a. Use the example data sheet(s); see pages 29 & 30.	
	39. Close the shutter.		
	40. Repeat steps 34 through 39 to obtain readings for the 6, 4, 2, and 0 mg/liter solutions and the sample, or the 0.6, 0.4, 0.2, and 0.0 mg/liter solutions, and the sample.		

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
G. Analysis (continued)			
	41. Replace the beaker of sample with the beaker of deionized water.		
	42. Allow the deionized water to aspirate for 10 seconds.		
	43. Swing the beaker of deionized water out of the burner housing.		
	44. Close the main valve on the hydrogen cylinder.	44a. By turning clockwise all the way.	
	45. When the hydrogen pressure registers 0 on the control panel hydrogen (fuel) gauge, close the main valve on the oxygen cylinder.	45a. By turning clockwise all the way.	
	46. Turn the sensitivity knob to the standby position.		
	47. Turn off the power toggle switch.		
	48. Empty all of the small beakers used.	48a. Don't forget the one still in the instrument. 48b. If the beakers are of the disposable type, discard them and proceed to H. If they are glass, do steps 49, 50, and 51.	
	49. Rinse the beakers thoroughly with tap water.		
	50. Rinse the beakers thoroughly with deionized water.		

OPERATING PROCEDURES	STEP SEQUENCE	INFORMATION/OPERATING GOALS/SPECIFICATIONS	TRAINING GUIDE NOTES
G. Analysis (continued)	51. Allow the beakers to drain dry, and then proceed to Section H.		
H. Calculations	1. For all of the standards, subtract the % transmittance obtained at the background wavelength from the % transmittance obtained at the peak wavelength.	1a. Example: 10.0 mg/liter solution 100 = % transmittance at the peak wavelength 1 = % transmittance at the background wavelength 99 = % transmittance difference	
	2. On "regular" graph paper prepare a calibration graph using the % transmittance differences along the vertical axis, and the corresponding concentrations (10, 8, 6, 4, 2, 0, or 1.0, 0.8, 0.6, 0.4, 0.2, 0.0 mg/liter) on the horizontal axis.	2a. If you have used both sets of standards (the intermediate and standard sodium solutions), prepare two calibration graphs. Pages 31 and 32 are sheets of "regular" graph paper. 2b. "Regular" graph paper is marked off in squares of equal size. 2c. EMP CH.IN.cg.EMP.1a.1.77 may be referred to for specific instructions in calibration graph preparation and use. 2d. In the case of the intermediate sodium solution, the calibration graph may have a slight bend.	
	3. Repeat step 1 for the sample.		
	4. Determine the sodium concentration in the sample.	4a. Using the calibration graph.	
	5. Record the result in mg/liter.	5a. Use the example data sheet(s); see pages 29 & 30.	

EXAMPLE
DATA SHEET

Concentration of Sodium Standards in mg/liter	% Transmittance at the Peak Wavelength; Peak Readings	% Transmittance at the Background Wavelength; Background Readings	% Transmittance Differences; Values in 2nd Column Minus Values in 3rd Col.
______*	______	______	______
______	______	______	______
______	______	______	______
______	______	______	______
______	______	______	______
______	______	______	______

Sample

Concentration of sodium in the sample in mg/liter ______

Peak Wavelength ________ nm

Background Wavelength ________ nm

* The six values in this column will be 0, 2, 4, 6, 8, and 10, or, 0.0, 0.2, 0.4, 0.6, 0.8, and 1.0. If both sets of standards were used, use a second data sheet exactly like this one; see page 30.

EXAMPLE
DATA SHEET
(See the paragraph at the bottom of Page 29)

Concentration of Sodium Standards in mg/liter	%Transmittance at the Peak Wavelength; Peak Readings	%Transmittance at the Background Wavelength; Background Readings	%Transmittance Differences; Values in 2nd Column Minus Values in 3rd Col.
______	______	______	______
______	______	______	______
______	______	______	______
______	______	______	______
______	______	______	______
______	______	______	______

Sample

Concentration of sodium in the sample in mg/liter _____

Peak Wavelength _________ nm
Background Wavelength _________ nm

EFFLUENT MONITORING PROCEDURE: Determination of Sodium Using Flame Photometry

TRAINING GUIDE

SECTION	TOPIC
I	Introduction
II	Educational Concepts - Mathematics
III	Educational Concepts - Science
IV	Educational Concepts - Communications
V*	Field and Laboratory Equipment
VI	Field and Laboratory Reagents
VII	Field and Laboratory Analysis
VIII	Safety
IX	Records & Reports

* Training guide materials are presented here under the headings marked *.

	TRAINING GUIDE NOTE	REFERENCES/RESOURCES
A.1.1	If the glassware is especially dirty and cannot be cleaned with ordinary detergents, chromic acid cleaning may be required.	
	1. Pour 35 ml of distilled water in a 250 ml beaker.	Standard Methods, 14th ed., P. 336, section 2c.2)
	2. Add about 1/8 teaspoon (simply estimate this quantity) of sodium dichromate, $Na_2Cr_2O_7$, to the water.	
	3. Swirl the beaker until the sodium dichromate has dissolved.	
	4. Keep repeating steps 2 and 3 until no more sodium dichromate will dissolve.	
	5. Pour the solution into a 2 liter beaker.	
	6. Slowly pour 1 liter of concentrated sulfuric acid, H_2SO_4, into the 2 liter beaker. Caution: Use eyeglasses and protective clothing.	
	7. Stir the mixture thoroughly.	
	8. Store it in a glass stoppered bottle.	
	9. The cleaning solution should be at a temperature of about 50°C when it is used.	
	10. It may therefore be necessary to warm the cleaning solution.	
	11. When using the warm cleaning solution, fill the piece of glassware with the solution.	
	12. Allow it to soak for 2-3 minutes (or longer).	
	13. Pour the cleaning solution back into the storage bottle.	
	14. Rinse the piece of glassware ten times with tap water.	
	15. The cleaning solution may be reused until it turns green.	
	16. It should then be discarded.	